

Review

Insight into Current Research on Luminescent Metal–Organic Frameworks (MOFs) Based on the 1,2,4-Triazole Scaffold

Kornelia Kubiesa  and Agnieszka Kudelko * 

Department of Chemical Organic Technology and Petrochemistry, The Silesian University of Technology, Krzywoustego 4, PL-44100 Gliwice, Poland; kornelia.kubiesa@polsl.pl

* Correspondence: agnieszka.kudelko@polsl.pl; Tel.: +48-32-237-17-29

Abstract

1,2,4-Triazoles, as heterocyclic compounds, represent an attractive class of ligands in the design of metal–organic frameworks (MOFs) due to their donor–acceptor character, thermal and chemical stability, and ability to form extended coordination networks. This review summarizes the literature published between 2019 and 2025 on luminescent MOFs incorporating 1,2,4-triazole scaffold. The analysis covers synthetic conditions and provides a detailed discussion of the luminescent properties of these materials. Particular emphasis is placed on their applicability as luminescent probes for environmental monitoring and medical diagnostics, as well as on their potential use in light-emitting diode construction. The collected data highlight promising results, including strong correlations between analyte concentration and luminescent response, enabling sensitive detection with low limits of detection (LOD) for selected analytes. This article may serve as a valuable resource for chemists, physicists, and engineers involved in the design of functional materials and the development of detection and optoelectronic technologies.

Keywords: 1,2,4-triazole; metal–organic framework; ions; cluster; luminescence; synthesis



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1. Introduction

Triazoles belong to the class of five-membered heterocyclic compounds composed of three nitrogen atoms and two sp^2 -hybridized carbon atoms. Depending on the arrangement of the heteroatoms within the cyclic system, two structural isomers can be distinguished, 1,2,3-triazole and 1,2,4-triazole (Figure 1), the latter being the subject of this article. For each structural isomer, three (A–C) and two tautomeric forms (D–E), respectively, can be identified (Figure 1) [1].

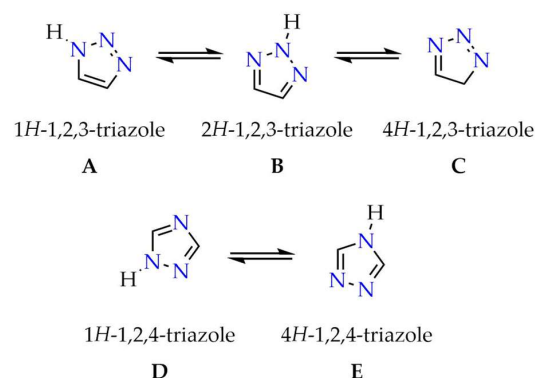


Figure 1. Structural isomers of triazole and their tautomeric forms.

Derivatives of 1,2,4-triazole have attracted increasing scientific interest over the years in the search for new solutions in fields such as medicine, agriculture, metallurgy, optoelectronics, and specialty materials chemistry. They are renowned for their exceptional biological activity, which arises from their ability to form hydrogen bonds and complex with metals, thereby enabling interactions with various biological targets such as enzymes [2,3]. Compounds containing the 1,2,4-triazole ring exhibit antibacterial [4], antiviral [5], antioxidant [6], antidepressant [7], anticancer [8] and antidiabetic properties [9]. Representative drugs of this class include Letrozole, used in breast cancer treatment [10], the antiviral Ribavirin [11], and Rizatriptan with antimigraine activity [12] (Figure 2). The 1,2,4-triazole ring is also present in agrochemical formulations marketed as fungicides and plant growth regulators, with examples including Paclobutrazol [13], Uniconazole [14], and Myclobutanil [15] (Figure 2).

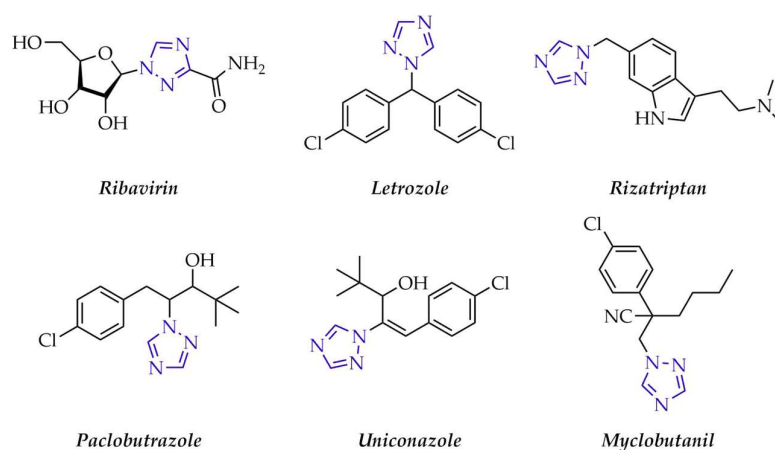


Figure 2. Representative drugs and pesticides that contain 1,2,4-triazole scaffold.

Triazoles also represent valuable molecular cores in the design of materials for optoelectronic devices such as organic light-emitting diodes (OLEDs). This can be achieved through the preparation of donor–acceptor compounds [16,17], or transition metal complexes [18,19]. Luminescent properties have also been reported for coordination polymers [20] and metal–organic frameworks (MOFs) based on 1,2,4-triazole. These systems may serve as luminescent thermometers or sensors sensitive to environmental pollutants such as metallic cations and anions, pharmaceuticals, pesticides, and nitroaromatic compounds (NACs). Furthermore, they may find application in medical diagnostics by indicating the presence of key biomarkers in human body fluids. Functionalization of the triazole ring leads to compounds with diverse applications. An example is 1,2,4-triazole-3-thiol derivatives, successfully employed as electrolytes in dye-sensitized solar cells (DSSCs) [21]. Tang and coworkers utilized a 3-amino-5-mercapto-1,2,4-triazole derivative to fabricate an electrode capable of detecting 3-caffeoylquinic acid—a phenolic acid responsible for preventing type 2 diabetes—in food and blood samples under physiological conditions [22]. Bakov and coworkers developed a 1,2,4-triazole conjugate with a 1,8-naphthalimide fluorophore, which functions as a fluorescent probe sensitive to toxic volatile amines, particularly ammonia [23]. Due to their high nitrogen content, triazole-based compounds are widely applied in energetic materials [24], for instance, in the form of energetic ionic liquids (EILs) [25]. Owing to their ability to form weak interactions with steel surfaces, certain 1,2,4-triazoles generate protective films against corrosive agents, which is of particular importance in metallurgy [26,27]. The structures of the triazole units used in the described examples are shown in Figure 3.

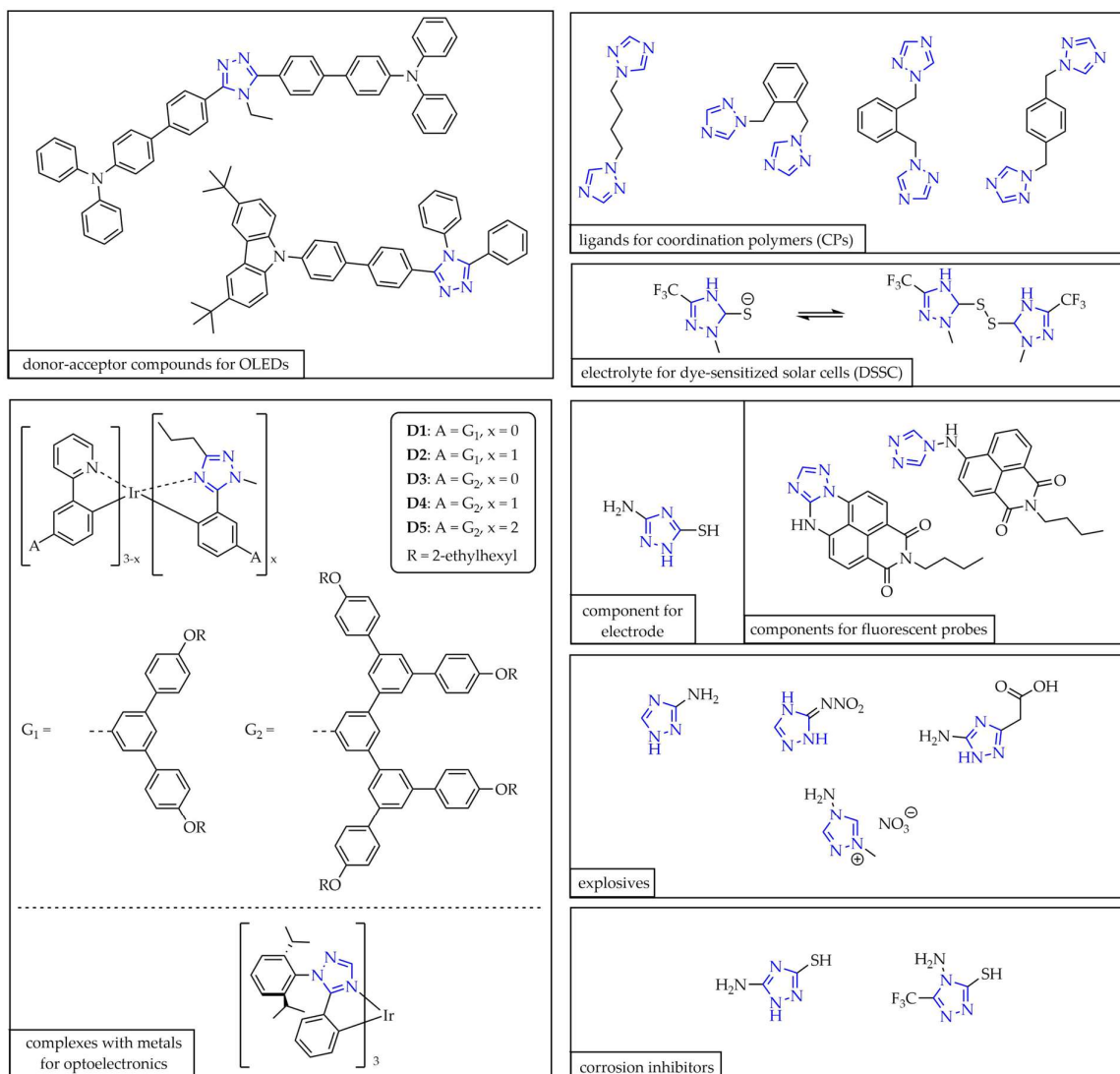


Figure 3. Selected 1,2,4-triazoles for various purposes: optoelectronic applications, materials science, high-energy-density materials, medical diagnostics, and metallurgy.

In this review, we highlight selected synthetic approaches to the 1,2,4-triazole scaffold, taking into account its two tautomeric forms: 1*H*-1,2,4-triazole and 4*H*-1,2,4-triazole. The first literature reports on the synthesis of metal–organic frameworks incorporating a 1,2,4-triazole moiety within their structure appeared in 2004. Since then, and particularly in recent years, interest in such derivatives has been steadily increasing, as reflected by the growing number of related publications. The main focus of this review is to provide a systematic summary of scientific reports from recent years (2019–2025) concerning the preparation of metal–organic frameworks (MOFs) incorporating ligands based on this heterocyclic motif. Particular attention is paid to the luminescent properties of these materials and potential possibilities for their practical application. The subject matter has an interdisciplinary character, as it combines achievements from many scientific fields, including organic chemistry, inorganic chemistry, coordination chemistry, physics, biotechnology, and materials engineering. By presenting the most recent advances, this article aims to provide comprehensive knowledge to researchers working across different disciplines, highlighting the exceptional application potential of luminescent metal–organic frameworks (LMOFs).

2. Selected Methods for Obtaining 1,2,4-Triazoles

2.1. Synthesis of 1*H*-1,2,4-Triazoles

One of the tautomeric forms, 1*H*-1,2,4-triazole, can be obtained through a number of different methodologies, some of which are presented in Figure 4 (**methods A–H**). As described by Chen and coworkers (**method A**) [28], the substrates in the transformation leading to the 1,2,4-triazole ring may include hydrazone derivatives and aliphatic amines. The authors employed aerobic oxidation conditions in the presence of molecular iodine and *tert*-butyl hydroperoxide (TBHP) as oxidant, without the participation of transition metals. This cascade reaction proceeded through a sequence of subsequent transformations involving C–H functionalization, C=N double bond formation, and oxidative aromatization. Lee and coworkers developed a method for the synthesis of trisubstituted 1,2,4-triazole derivatives from *N*-acylated amides and various hydrazine hydrochlorides using microwave irradiation (**method B**) [29]. This approach enabled the desired products to be obtained within a few minutes, with good yields up to 88%. They also described a rapid and efficient one-pot method tested with various benzamide derivatives as starting materials. **Method C** presents the approach developed by Castanedo and coworkers, in which carboxylic acids and primary amidines were used as substrates [30]. These were subjected to the coupling reagent hexafluorophosphate azabenzotriazole tetramethyl uronium (HATU) and *N,N*-diisopropylethylamine (DIPEA) as base, yielding an acylamidine intermediate. In the subsequent step, it reacted with a monosubstituted hydrazine derivative, and within 1–3 h, the cyclic main product was formed. 1*H*-1,2,4-Triazoles can also be synthesized electrochemically from hydrazone and amidine derivatives in the presence of potassium iodide, as reported by Jiang and coworkers (**method D**) [31]. This strategy afforded a series of products bearing both alkyl and aryl substituents, with moderate to good yields, without the need for chemical oxidants. Huang and coworkers obtained 1,3-disubstituted 1,2,4-triazole derivatives via catalytic C(*sp*³)–H functionalization of amidines. They used a catalytic system consisting of copper(I) iodide (CuI), atmospheric oxygen as oxidant, and tripotassium phosphate (K₃PO₄) as base (**method E**) [32]. The authors described the synthesis of a series of triazole derivatives in good yields ranging from 72% to 92%. The 1,2,4-triazole ring may also be obtained via [3+2] cycloaddition of isocyanides and diazonium salts (**method F**). Liu and coworkers investigated this method and reported the influence of the catalyst on the regioselectivity of the reaction [33]. Formation of 1,3-disubstituted 1,2,4-triazole was observed when silver(I) carbonate (Ag₂CO₃) was used as catalyst (also acting as a base), whereas 1,5-disubstituted 1,2,4-triazole was obtained in the presence of copper(II) acetate (Cu(OAc)₂) and lithium acetate (LiOAc) as base. **Method G** describes the synthesis of 1,3,5-trisubstituted 1,2,4-triazoles via base-promoted [3+2] dipolar cycloaddition of trifluoroacetohydrazonoyl chlorides with imides [34]. This procedure, reported by Zhang and coworkers, led to the desired trifluoromethyl-substituted triazole derivatives in excellent yields (91–99%) and high regioselectivity. Another approach (**method H**) involves a two-step heterocyclization comprising amination and cyclization of hydrazonamide with an acid chloride in the presence of triethylamine (TEA) [35]. This procedure, employed by Li and coworkers, was used to synthesize bioactive 1-aryl-1*H*-1,2,4-triazole-3-carboxylate derivatives, which were subsequently evaluated for their ability to inhibit nitric oxide (NO) production and cyclooxygenase COX-1/COX-2 activity.

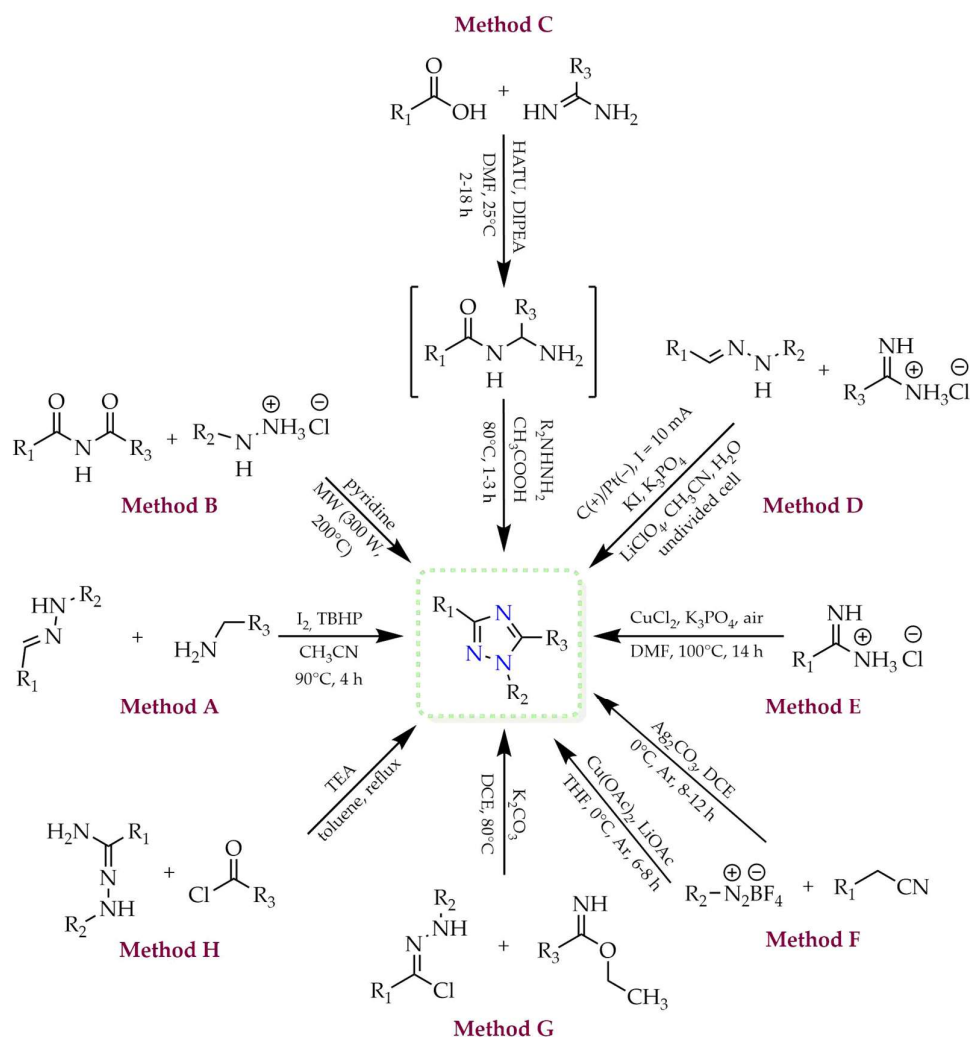


Figure 4. Various methods for the preparation of 1H-1,2,4-triazole ($R_1, R_2, R_3 = H, \text{alkyl, aryl, } NH_2, CF_3, COOCH_3, \text{etc.}$).

2.2. Synthesis of 4H-1,2,4-Triazoles

The preparation of 4H-1,2,4-triazole derivatives requires the use of different starting materials and procedures compared to the 1H-1,2,4-triazole tautomer. Possible approaches to their synthesis are presented in Figure 5 (methods I–P). By selecting the appropriate method, it is possible to control the formation of one of these tautomeric structures. **Method I**, described by Olesiejuk and coworkers, involves the reaction of a diimidoyl dichloride derivative with an amine in boiling toluene, leading to cyclization and the formation of the 4H-1,2,4-triazole ring [36]. Using this procedure, precursor compounds were obtained, which were then subjected to Suzuki cross-coupling, resulting in derivatives exhibiting luminescent properties. Another synthetic approach involves the addition of hydrazides to secondary amides (**method J**) [37]. Bechara and coworkers developed an efficient one-pot method for this transformation, applying an amide activation strategy using trifluoromethanesulfonic anhydride (Tf₂O) in the presence of 2-fluoropyridine (2-FPy) as a base. In the subsequent step, the cyclodehydration process was induced by microwave irradiation. **Method K** relies on oxidative cyclization of various trifluoroacetimidoyl hydrazide derivatives and *N,N*-dimethylformamide (DMF) mediated by iodine (I₂) [38]. Using this method, Lu and coworkers obtained a series of derivatives with yields ranging from 42 to 62% and demonstrated their application potential by synthesizing a key structural element of an anti-coagulant drug acting as factor IXa inhibitor. The reaction between dimethylcyanamide and anhydrous hydrazine also allows for the construction of the 1,2,4-triazole ring, as reported

by Yocca and coworkers (**method L**) [39]. **Method M** involves the intramolecular cyclization of hydrazine-1-carbothioamide derivative, which proceeds in an aqueous sodium hydroxide solution [40]. As reported by Rahim and coworkers, after neutralization of the medium with dilute hydrochloric acid, the desired 1,2,4-triazole derivative was successfully isolated. **Method N**, described by Hutchinson and coworkers, consists of the reaction of an amine with *N'*-((dimethylamino)methylene)-*N,N*-dimethylformohydrazoneamide in an acidic medium generated by the addition of *p*-toluenesulfonic acid, resulting in substituted 1,2,4-triazole derivatives [41]. Such a moiety was also obtained, as reported by Gogoi and coworkers, from arylidenearylthiosemicarbazides in a Cu(II)-catalyzed reaction carried out in DMSO at 80 °C (**method O**) [42]. Using this procedure, two groups of heterocycles were obtained: 4,5-disubstituted 1,2,4-triazole-3-thiones, which upon extended reaction time underwent desulfurization to the corresponding 4,5-disubstituted 1,2,4-triazole derivatives. Oxidative cyclization of amidrazones and aldehydes also leads to the formation of the 4*H*-1,2,4-triazole system (**method P**). This was reported by Nakka and coworkers, who used ceric ammonium nitrate (CAN) as the oxidizing agent and polyethylene glycol as the reaction medium [43]. This way a series of 3,4,5-trisubstituted 1,2,4-triazole derivatives was successfully obtained in high yields (87–97%).

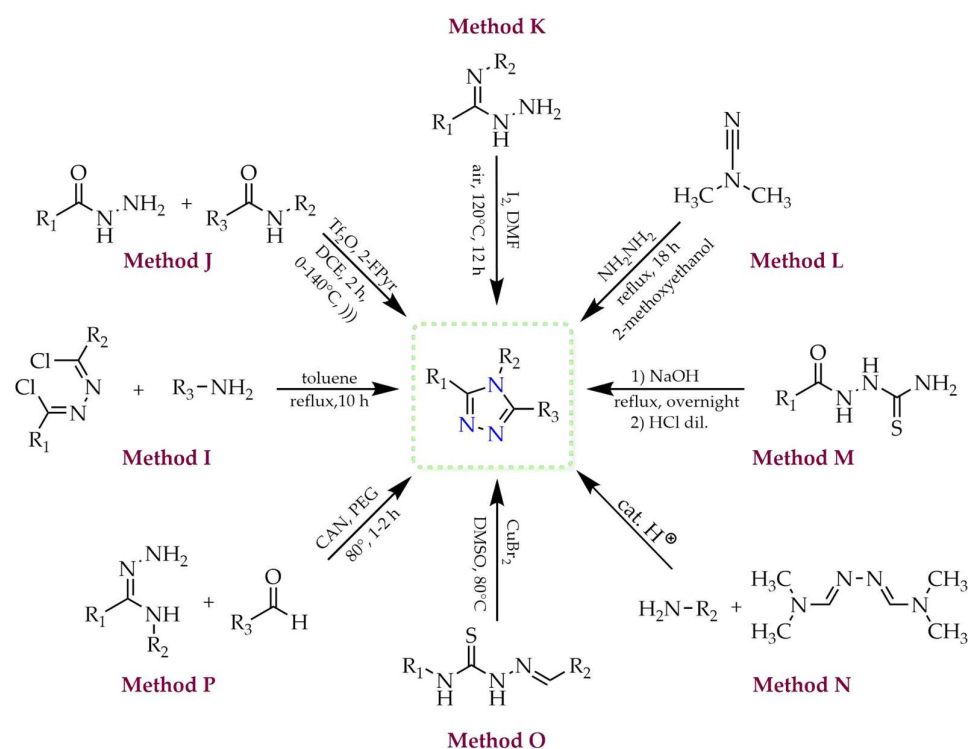


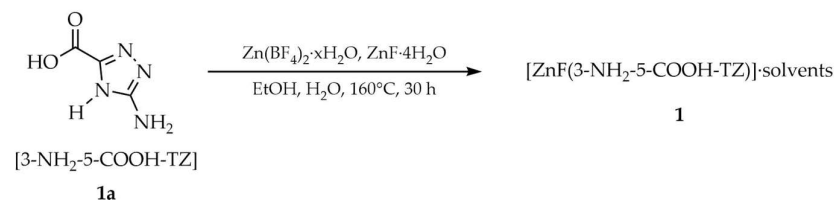
Figure 5. Various methods for the preparation of 4*H*-1,2,4-triazole ($R_1, R_2, R_3 = \text{H, alkyl, aryl, CF}_3, \text{SH, etc.}$).

3. Triazole-Based Luminescent Metal—Organic Frameworks (LMOFs)

3.1. Metal—Organic Frameworks (MOFs)

Metal–organic frameworks (MOFs) represent a class of solid polymeric materials at the intersection between materials science and coordination chemistry. They are composed of metal ions or metal clusters, which act as nodes in the structure. Organic ligands connect these coordination centers, resulting in the formation of one-, two- or three-dimensional networks. Proper selection of linkers and nodes enables the preparation of functional materials with desired properties [44]. The first literature report on the application of a 1,2,4-triazole derivative for the construction of metal–organic frameworks dates back

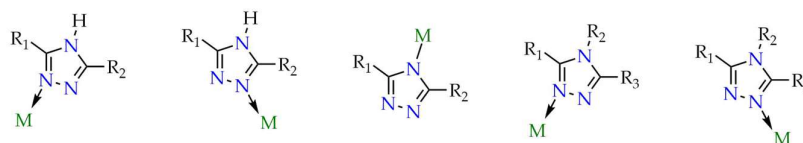
to 2004. Su and coworkers published an article in which they obtained a MOF with the formula $[\text{ZnF}(\text{3-NH}_2\text{-5-COOH-TZ})]\cdot\text{solvents}$ (**1**), using a solvothermal approach. The synthesis employed heating of 3-amino-1,2,4-triazole-5-carboxylic acid hemihydrate ($[\text{3-NH}_2\text{-5-COOH-TZ}]$, **1a**), zinc(II) tetrafluoroborate hydrate, and zinc(II) fluoride tetrahydrate in aqueous ethanol for 30 h (Scheme 1) [45].



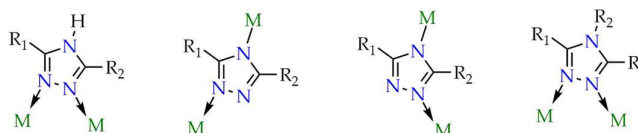
Scheme 1. Synthesis of the first 1,2,4-triazole-based MOF described in the literature.

Ligands based on a triazole core are increasingly used for MOF construction. Important characteristics of linkers that influence the physicochemical properties of the material, apart from their size and shape, include the number of potential coordination sites. The greater the number of such sites, the greater the diversity of networks that can be obtained. This is achieved either by introducing coordination-capable functional groups, such as carboxyl or amino groups, or by designing the ligand structure around heterocycles such as pyridine, imidazole, etc. For this reason, the triazole ring represents an attractive structural motif as it contains three nitrogen atoms that can act as potential binding sites in coordination networks with metals, as illustrated in Figures 6 and 7.

Monodentate:



Bidentate:



Tridentate:

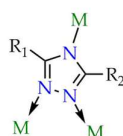
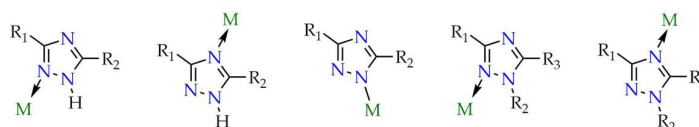


Figure 6. Possible coordination modes for 4H-1,2,4-triazole derivatives (R_1 , R_2 , R_3 = alkyl, aryl, pyridyl, isophthalic acid, etc.).

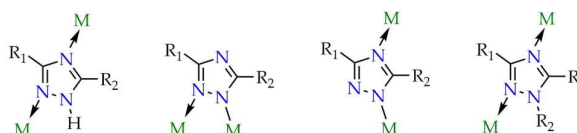
The construction of networks containing organic ligands and metal nodes requires suitable conditions that enable the formation of coordination bonds. The literature describes numerous methodologies for MOF's preparation, including microwave-assisted, sonochemical, electrochemical, and mechanochemical methods [46]. Well-known MOFs such as MOF-5, MOF-74, MOF-177, and MOF-199 have been obtained by mixing starting materials at room temperature [47]. The most important methods for obtaining luminescent 1,2,4-triazole-based MOFs are solvothermal and hydrothermal approaches. These are defined as reactions carried out in sealed vessels under pressure (greater than 1 atm) at a temperature above the boiling point of the solvent [48]. In the hydrothermal process,

the reaction takes place in the presence of water, while in the solvothermal process an additional organic solvent (protic or aprotic) is used [49,50].

Monodentate:



Bidentate:



Tridentate:

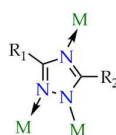
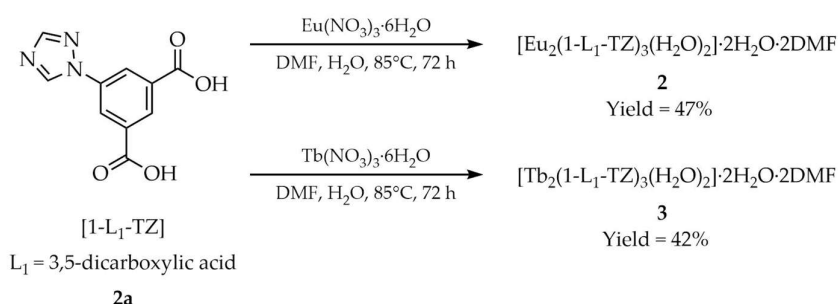


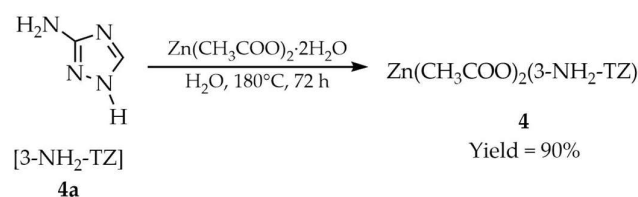
Figure 7. Possible coordination modes for 1*H*-1,2,4-triazole derivatives (R_1 , R_2 , R_3 = alkyl, aryl, pyridyl, isophthalic acid, etc.).

For example, Sun and coworkers described a solvothermal approach to the synthesis of lanthanide-based MOFs [51]. Europium(III) and terbium(III) nitrate pentahydrates ($\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ln} = \text{Eu}, \text{Tb}$) and 5-(1*H*-1,2,4-triazol-1-yl)isophthalic acid ([1- L_1 -TZ, L_1 = 3,5-dicarboxylic acid)], **2a**, Scheme 2) were employed as starting materials. Substrates (0.1 mmol) were placed in a Teflon-lined stainless-steel container together with 4 mL of water and DMF. The vessel was tightly sealed and heated at 85 °C for 72 h, then cooled to room temperature under ambient conditions. Colorless crystals of $[\text{Eu}_2(1-L_1\text{-TZ})_3(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O} \cdot 2\text{DMF}$ (**2**) and $[\text{Tb}_2(1-L_1\text{-TZ})_3(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O} \cdot 2\text{DMF}$ (**3**) were filtered off, washed with DMF, and air-dried. The products were obtained in yields of 47% and 42%, respectively.



Scheme 2. Synthesis of lanthanide-based MOFs by solvothermal approach.

In turn, Liu and coworkers employed hydrothermal conditions to synthesize a zinc-based MOF with the formula $\text{Zn}(\text{CH}_3\text{COO})_2(\text{L})$ (**4**, Scheme 3) [52]. For this synthesis, zinc(II) acetate dihydrate, 3-amino-1,2,4-triazole ([3- NH_2 -TZ], **4a**) and water were used. The reaction was carried out in a sealed vessel at 180 °C for 72 h. Pure crystals were obtained in 90% yield.



Scheme 3. Synthesis of a Zn-based MOF by hydrothermal approach.

An important issue after isolating a MOF product from the reaction mixture is the confirmation of its composition [53], which is typically performed by means of elemental analysis and infrared (IR) spectroscopy. In addition, determining its crystal structure is essential, which is achieved through X-ray crystallography. The percentage content of metallic components is determined using inductively coupled plasma mass spectrometry (ICP-MS). Scanning electron microscopy (SEM) analysis enables high-resolution imaging of the material's surface. For MOFs with optoelectronic applications, the required properties include high thermal and chemical stability [54]. For this purpose, thermogravimetric analysis (TG) is employed, belonging to the family of thermal analysis methods, allowing observation of changes in physical properties as a function of temperature or time. Structural stability during aging processes and after exposure to different solvents is assessed by powder X-ray diffraction (PXRD). Porosity and specific surface area are determined based on nitrogen sorption isotherms and using the Brunauer–Emmett–Teller (BET) model [55]. In the preparation of luminescent probes, this method is used to assess the possibility of regeneration and reusability of the probe. Analyses employed to determine luminescent properties include UV–Vis spectroscopy and photoluminescence (PL) spectroscopy [56].

The working principle of luminescent probes constructed on the basis of MOFs lies in the fact that the analyte can induce an “turn-on” effect or luminescence enhancement, which is quantitatively described by the enhancement constant (K_{EC}). However, the most commonly observed phenomenon is luminescence “turn-off” or quenching, for which the Stern–Volmer constant (K_{SV}) is determined. An important parameter describing the sensitivity of the probe is the limit of detection (LOD), defined based on the obtained constant, which indicates the lowest concentration of analyte that can be detected using the material. Numerous mechanisms of analyte detection by coordination porous materials have been reported in the literature, where the response is reflected in changes in the luminescence spectrum. These include photoelectron transfer (PET), resonance energy transfer (RET), competition absorption (CA), chemical conversion (CC), and structural transformation (ST) [57].

Metal–organic frameworks exhibit many other properties attractive for applications, among which their porosity deserves special attention, as it enables storage and transport of guest molecules. They also feature high thermal stability [44,58,59]. The appropriate pore size and developed surface area allow adsorption and storage of gases such as hydrogen (H_2) [60], methane (CH_4) [61], and acetylene (C_2H_2) [62]. Morphological aspects also enable selective gas separation, e.g., methane from nitrogen (CH_4/N_2) [63], ethylene (C_2H_4) from CO_2 or C_2H_2 [62], as well as in ternary mixtures [64], and CO_2 from N_2 , H_2 , and CH_4 [65]. Promising results have also been obtained for selective capture of toxic gases such as sulfur dioxide (SO_2) [66], nitrogen dioxide (NO_2) [66], hydrogen sulfide (H_2S) [67] and ammonia (NH_3) [68]. This phenomenon has also been exploited for water capture from air in the development of water sorption-driven devices [69]. The structures of metal–organic frameworks contain metallic nodes that can act as catalytic sites, making them applicable in heterogeneous catalysis [70,71]. Their porosity also allows encapsulation of guest molecules that serve as additional catalytic centers, such as metallic nanoparticles or enzymes [72]. They can be used not only in thermal catalysis but also in reactions

where they act as electro- [73] or photocatalysts [74]. Metal–organic frameworks represent a promising class of materials for advanced biomedical applications, such as targeted drug delivery systems, diagnostic imaging techniques, and radio- and phototherapy. MOFs have been studied as contrast agents for magnetic resonance imaging (MRI) [75] and computed tomography (CT) [76]. The possibility of exchanging metal nodes in structural networks enables the preparation of MOFs containing positron-emitting radioisotopes, which can be successfully detected by positron emission tomography (PET) [77]. Frameworks incorporating components capable of absorbing exogenous energy in the form of light or X-rays can convert it to trigger localized therapeutic effects in photodynamic therapy (PDT) [78] and radiotherapy–radiodynamic therapy (RT-RDT) [79]. High porosity and suitable adsorption/release profiles of active substances allow the development of efficient drug delivery systems, which are particularly important for targeted therapy [80]. MOFs can also be designed as optical sensors, whose operation is based on solvatochromic [81] or luminescent [82] effects. Furthermore, they have been applied in the development of electromechanical sensors [83], chemiresistive sensors [84], electrochemical sensors [85], and chemicapacitors [86]. Their potential use in chemically sensitive field-effect transistors (ChemFETs) has also been demonstrated [87]. An interesting approach involves creating cross-reactive arrays, enabling the discrimination of multiple analytes in multicomponent mixtures [88]. Finally, MOFs are a promising class of materials for energy-related applications, such as batteries and supercapacitors [89].

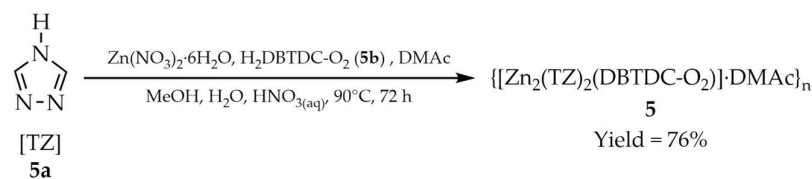
In the following subsections, 1,2,4-triazole-based LMOFs constructed with metals such as zinc, cadmium, and lanthanides including europium, gadolinium, terbium, lanthanum, holmium, and dysprosium, as well as metal clusters and frameworks containing cobalt, copper, and lead, are described. Fundamental data on their luminescent properties, including absorption, excitation, and emission wavelengths, are summarized in Tables 1–5. Particular attention is given to their potential for luminescent sensing of various analytes, with quenching or enhancement constants and detection limits provided. Table 6 summarizes these parameters for the detection of cations and anions, while Table 7 presents the corresponding data for organic compounds, whose structures are shown in Figure 8. For some of the obtained MOFs, the quantum yield and luminescence lifetime were determined, and these results are summarized in Table 8.

3.1.1. Zinc-Based Metal–Organic Frameworks Containing 1,2,4-Triazole Organic Linker

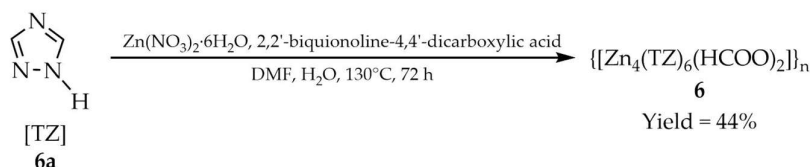
One of the most widely employed metal ions for the construction of 1,2,4-triazole-based MOFs is zinc. In 2019, two studies were reported on this subject. He and coworkers described the synthesis of a three-dimensional porous framework, $\{[\text{Zn}_2(\text{TZ})_2(\text{DBTDC-O}_2)]\cdot\text{DMAc}\}_n$ (**5**, Scheme 4), obtained from two organic ligands: 4*H*-1,2,4-triazole (HTZ, **5a**) and *S,S*-dioxodibenzothiophene-3,7-dicarboxylic acid ($\text{H}_2\text{DBTDC-O}_2$, **5b**) in a dimethylacetamide (DMAc) medium [90]. Compound **5** exhibits high water stability across a broad pH range (3–12) and, through luminescence quenching or enhancement, functions as a versatile sensor for detecting metal cations (Fe^{3+} , Al^{3+}), anions (SiF_6^{2-} , $\text{Cr}_2\text{O}_7^{2-}$) (Table 6, Entry 1), and even antibiotics such as nitrofurantoin (NFT) and nitrofurazone (NFZ) (Table 7, Entry 1). In order to reveal the porosity of the material, a nitrogen sorption isotherm was also measured at 77 K.

Zou and coworkers reported the solvothermal synthesis of $\{[\text{Zn}_4(\text{TZ})_6(\text{HCOO})_2]\}_n$ (**6**, Scheme 5), based on the tautomeric 1*H*-1,2,4-triazole (TZ, **6a**) [91]. Here, 2,2'-biquinoline-4,4'-dicarboxylic acid did not coordinate Zn^{2+} ions directly but facilitated framework formation, while formate anions incorporated into the MOF skeleton originated from the decomposition of *N,N*-dimethylformamide (DMF). The resulting material displayed both thermal and aqueous stability. Owing to its luminescent properties (Table 1), framework

6 was demonstrated to act as a luminescent sensor sensitive to $\text{Cr}_2\text{O}_7^{2-}$ ions (Table 6, Entry 2).

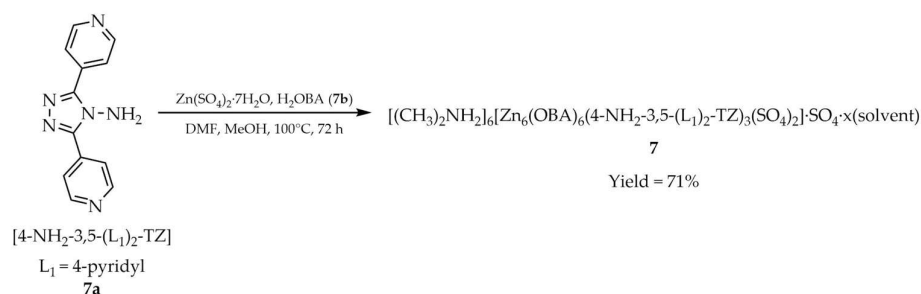


Scheme 4. Synthesis of a zinc-based MOF (**5**) from 4H-1,2,4-triazole (**5a**) and S,S-dioxodibenzothiophen-3,7-dicarboxylic acid (**5b**).



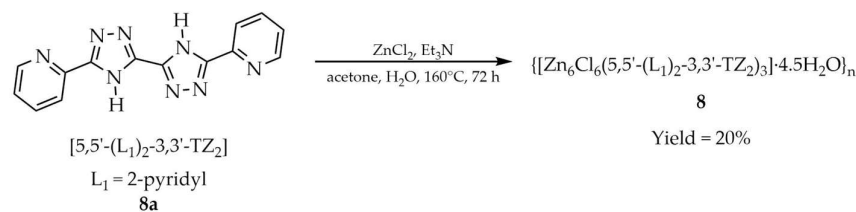
Scheme 5. Preparation of a Zn-based MOF (**6**) from 1H-1,2,4-triazole (**6a**) and 2,2'-biquionoline-4,4'-dicarboxylic acid.

In 2020, Qin and coworkers synthesized another Zn-based MOF, $[(\text{CH}_3)_2\text{NH}_2]_6[\text{Zn}_6(\text{OBA})_6(4\text{-NH}_2\text{-}3,5\text{-(L}_1)_2\text{-TZ)}_3(\text{SO}_4)_2] \cdot \text{SO}_4 \cdot x(\text{solvent})$ (**7**, Scheme 6), employing 4-amino-3,5-bis(4-pyridyl)-1,2,4-triazole ($[4\text{-NH}_2\text{-}3,5\text{-(L}_1)_2\text{-TZ}]$, $\text{L}_1 = 4\text{-pyridyl}$, **7a**), 4,4'-oxybis(benzoic acid) (H_2OBA , **7b**), and hydrated zinc sulfate [92]. This compound, due to the correlation of luminescence intensity and temperature, has the potential to be used as a thermal sensor. Temperature-dependent emission spectra were recorded between 87 and 277 K, revealing a gradual decrease in luminescence intensity with increasing temperature. Furthermore, compound **7** demonstrated the ability to detect and quantify Ni^{2+} and PO_4^{3-} ions in aqueous solution (Table 6, Entry 3).



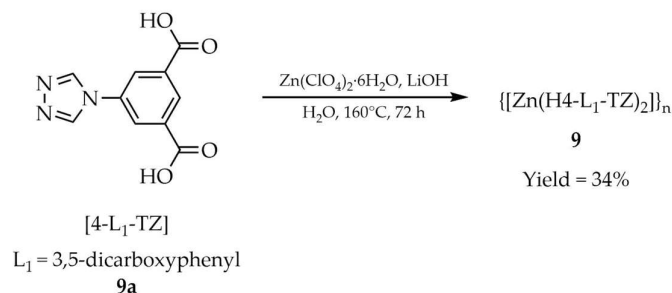
Scheme 6. Synthesis of a zinc-based MOF (**7**) from 4-amino-3,5-bis(4-pyridyl)-1,2,4-triazole (**7a**) and $\text{H}_2\text{OBA} = 4,4'\text{-oxybis(benzoic acid)}$ (**7b**).

Cao and coworkers reported a novel three-dimensional Zn-based framework constructed from the ligand 5,5'-di(pyridin-2-yl)-3,3'-bi(1,2,4-triazole) ($[5,5'\text{-(L}_1)_2\text{-}3,3'\text{-TZ}_2]$, $\text{L}_1 = 2\text{-pyridyl}$, **8a**, Scheme 7) [93]. The material, formulated as $\{[\text{Zn}_6\text{Cl}_6([5,5'\text{-(L}_1)_2\text{-}3,3'\text{-TZ}_2)_3] \cdot 4,5\text{H}_2\text{O}]\}_n$ (**8**) was obtained under solvothermal conditions in a water–acetone medium. Both thermal and chemical stability were confirmed. Solid-state luminescence tests in the presence of various cations and anions revealed that compound **8** functions as a sensitive and efficient fluorescent sensor for Cu^{2+} , Ag^+ , MnO_4^- , and Cr(VI) species ($\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-}) (Table 6, Entry 4). Importantly, the sensor could be rapidly regenerated and reused for at least four detection cycles.



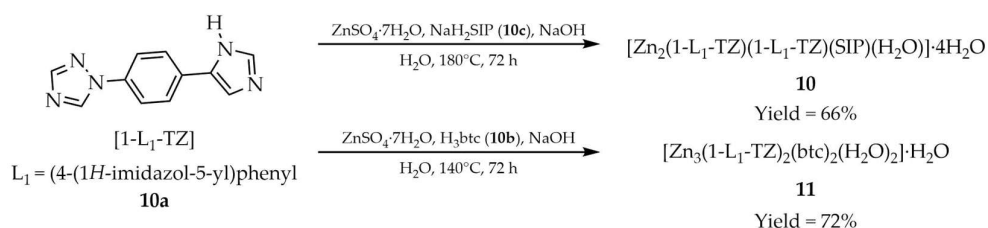
Scheme 7. Preparation of a Zn-based MOF (**8**) using 5,5'-di(pyridin-2-yl)-3,3'-bi(1,2,4-triazole) (**8a**).

Another Zn-MOF reported by Liu and co-workers displayed luminescent properties (Table 1) and also served as an efficient heterogeneous catalyst for the Knoevenagel condensation between benzaldehyde derivatives and malononitrile [94]. Framework $\{[Zn(H_4-L_1-TZ)_2]\}_n$ (**9**, Scheme 8) was obtained hydrothermally from 5-(4*H*-1,2,4-triazol-4-yl)isophthalic acid ($[4-L_1-TZ]$, $L_1 = 3,5\text{-dicarboxyphenyl}$, **9a**), hydrated zinc perchlorate, lithium hydroxide, and water. Anion-sensing studies in aqueous media revealed that compound **9** exhibited the strongest luminescence response toward CN^- ions, compared with F^- , Cl^- , Br^- , CH_3COO^- , NO_3^- , $H_2PO_4^-$, and HSO_4^- . Notably, luminescence enhancement was observed in the presence of cyanide, although the enhancement constant (K_{EC}) and limit of detection (LOD) were not reported.



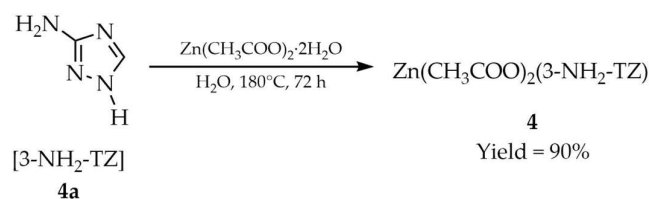
Scheme 8. Synthesis of a zinc-based MOF (**9**) employing 5-(4*H*-1,2,4-triazol-4-yl)isophthalic acid (**9a**).

In another study, Li and coworkers employed 1-(4-(1*H*-imidazole-5-yl)phenyl)-1*H*-1,2,4-triazole ($[1-L_1-TZ]$, $L_1 = (4-(1H\text{-imidazole-5-yl)phenyl})$, **10a**, Scheme 9), 1,2,3-benzenetricarboxylic acid ($H_3\text{btc}$, **10b**), and sodium 5-sulfoisophthalate (NaH_2SIP , **10c**) as ligands for the synthesis of four MOFs based on zinc, manganese, and cadmium [95]. Two of the zinc-containing products displayed luminescent properties: $[Zn_2(1-L_1-TZ)(1-L_1-TZ)(SIP)(H_2O)] \cdot 4H_2O$ (**10**) and $[Zn_3(1-L_1-TZ)_2(btc)_2(H_2O)_2] \cdot H_2O$ (**11**) (Table 1). The reactions were performed in aqueous media with sodium hydroxide as base, and hydrated zinc sulfate as the metal source. Interestingly, the same reagents afforded different framework compositions depending on the reaction temperature: 180 °C for **10** and 140 °C for **11**. Among the obtained MOFs, compound **10** exhibited the highest thermal stability and the most intense luminescence, with a quantum yield of 5.24% and the longest emission lifetime (29.56 ns). For compound **11**, the quantum yield and emission lifetime were determined to be 3.18% and 18.53 ns, respectively.



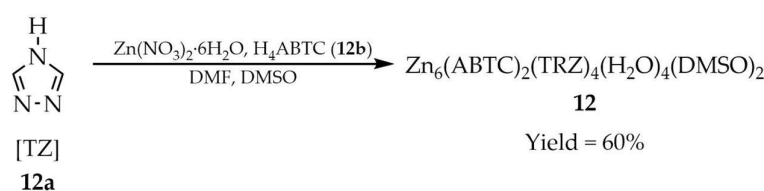
Scheme 9. Preparation of two zinc-based MOFs (**10**, **11**) using 1-(4-(1*H*-imidazole-5-yl)phenyl)-1*H*-1,2,4-triazole (**10a**), 1,2,3-benzenetricarboxylic acid (**10b**) and sodium 5-sulfoisophthalate (**10c**).

Liu and coworkers reported the synthesis and characterization of a novel two-dimensional zinc-based MOF, $\text{Zn}(\text{CH}_3\text{COO})_2(3\text{-NH}_2\text{-TZ})$ (**4**, Scheme 10), constructed from 3-amino-1,2,4-triazole ([3-NH₂-TZ] **4a**) [52]. The material was obtained via hydrothermal treatment of zinc acetate hydrate with 3-amino-1,2,4-triazole at 180 °C. Luminescence studies revealed strong blue emission at 433 nm upon excitation at 382 nm (Table 1). A weaker green emission (487–600 nm) corresponded to long-persistent luminescence (LPL), with an afterglow lasting up to ~3 s.



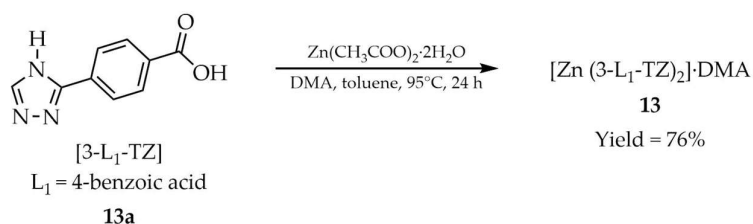
Scheme 10. Synthesis of a zinc-based MOF (**4**) employing 3-amino-1,2,4-triazole (**4a**).

Rui-Ying Yu and coworkers described the synthesis and characterization of a Zn-MOF with the formula $\text{Zn}_6(\text{ABTC})_2(\text{TZ})_4(\text{H}_2\text{O})_4(\text{DMSO})_2$ (**12**, Scheme 11), employing unsubstituted 1,2,4-triazole ([TZ], **12a**), and 3,3',5,5'-azobenzenetetracarboxylic acid (H_4ABTC , **12b**) as ligands [96]. The synthesis was carried out in polar solvents such as dimethylformamide (DMF) and dimethylsulfoxide (DMSO). UV-Vis analysis showed that compound **12** exhibited an absorption band at 337 nm, which is a slight red shift compared to the free ligand **12b** (Table 1). It shows strong blue emission with chromaticity coordinates (CIE) of (0.1363, 0.2079), suggesting its potential for LED applications.



Scheme 11. Preparation of a zinc-based MOF (**12**) from 1,2,4-triazole (**12a**) and 3,3',5,5'-azobenzenetetracarboxylic acid (**12b**).

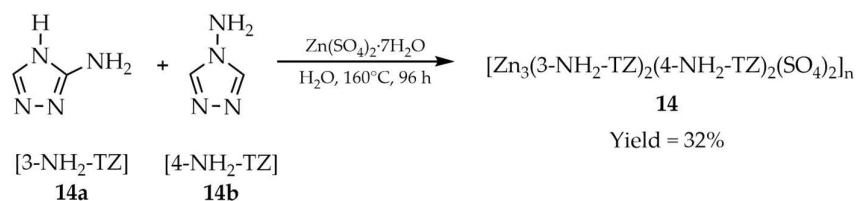
In the same year, Fang and coworkers reported the synthesis and properties of a luminescent zinc-based MOF, $[\text{Zn}(3\text{-L}_1\text{-TZ})_2] \cdot \text{DMA}$ (**13**, Scheme 12), derived from 4-(1H-1,2,4-triazol-1-yl)benzoic acid ([3-L₁-TZ, L₁ = 4-benzoic acid, **13a**) and zinc acetate dihydrate in medium composed of *N,N*-dimethylacetamide (DMA) and toluene [97]. The authors investigated the use of product **13** as a bifunctional luminescent sensor for nitrobenzene (NB) (Table 7, Entry 2) and Fe^{3+} ions (Table 6, Entry 5). Compound **13** displayed blue-violet luminescence with a quantum yield of 7.4%. Gas sorption analysis revealed selective adsorption of CO_2 at 195 K, with a type I isotherm typical for microporous materials.



Scheme 12. Synthesis of a zinc-based MOF (**13**) from 4-(1H-1,2,4-triazol-1-yl)benzoic acid (**13a**).

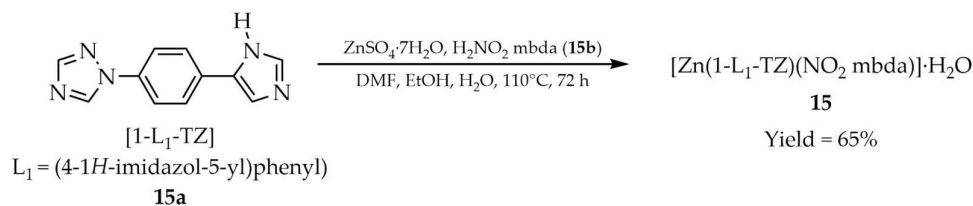
Another Zn-MOF constructed by Liu and coworkers, $[\text{Zn}_3(3\text{-NH}_2\text{-TZ})_2(4\text{-NH}_2\text{-TZ})_2(\text{SO}_4)_2]_n$ (**14**, Scheme 13), was synthesized solvothermally from $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and two

different aminotriazole ligands: 3-amino-1,2,4-triazole ([3-NH₂-TZ], **14a**) and 4-amino-1,2,4-triazole ([4-NH₂-TZ], **14b**) [98]. In addition to luminescent properties (Table 1), compound **14** exhibited high sensitivity and selectivity toward Fe³⁺ ions (Table 6, Entry 6).



Scheme 13. Preparation of a Zn-MOF (**14**) using 3-amino-1,2,4-triazole (**14a**) and 4-amino-1,2,4-triazole (**14b**).

Chen and coworkers described the synthesis of a Zn-MOF formulated as [Zn(1-L₁-TZ)(NO₂ mbda)]·H₂O (**15**, Scheme 14), using 1-(4-(1*H*-imidazol-5-yl)phenyl)-1*H*-1,2,4-triazole ([1-L₁-TZ, L₁ = (4-1*H*-imidazol-5-yl)phenyl], **15a**) and 5-nitroisophthalic acid (H₂NO₂ mbda, **15b**) as ligands [99]. The reaction was carried out in a mixture of solvents DMF/EtOH/H₂O using hydrated zinc sulfate. Luminescence properties were investigated (Table 1), and a luminescence lifetime of 8 ns was determined, with a quantum yield of 2.15%. Beyond zinc-based frameworks, the same review also discussed MOFs with magnetic properties based on other metals such as copper, cobalt, and manganese.

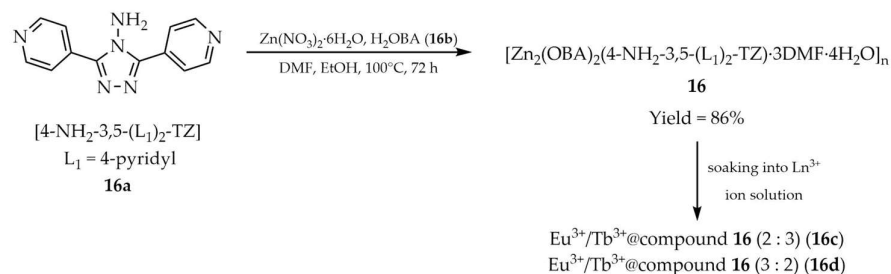


Scheme 14. Synthesis of a zinc-based MOF (**15**) from 1-(4-(1*H*-imidazol-5-yl)phenyl)-1*H*-1,2,4-triazole (**15a**) and 5-nitroisophthalic acid (**15b**).

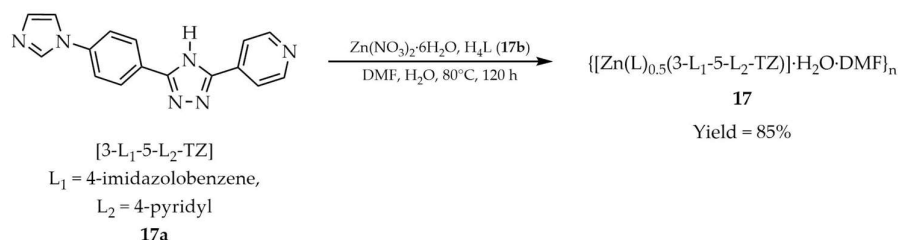
In 2022, Qin and coworkers used 4-amino-3,5-bis(4-pyridyl)-1,2,4-triazole ([4-NH₂-3,5-(L₁)₂-TZ, L₁ = 4-pyridyl, **16a**, Scheme 15) and 4,4'-oxybis(benzoic acid) (H₂OBA, **16b**) as ligands, resulting in the MOF [Zn₂(OBA)₂(4-NH₂-3,5-(L₁)₂-TZ)·3DMF·4H₂O]_n (**16**) [100]. The framework, obtained from zinc nitrate hexahydrate in DMF/EtOH solution, displayed an emission quantum yield of 18% and a luminescence lifetime of 6.27 ns. Product **16** functioned as a sensitive and selective sensor for Fe³⁺ and Cr₂O₇^{2−} ions (Table 6, Entry 7). Furthermore, it could act as a host for lanthanide ion encapsulation (Eu³⁺, Tb³⁺), enabling tuning of luminescent properties. Immersion of compound **16** in DMF containing Eu³⁺/Tb³⁺ (25 mM, 2:3 molar ratio) yielded Eu³⁺/Tb³⁺@compound **16** (2:3) (**16c**), which exhibited white-light emission with excellent CIE coordinates (0.32, 0.33), a moderate correlated color temperature (CCT) of 6180 K, and an absolute quantum yield of 25.3%. The corresponding luminescence lifetimes were 484.5 μs and 1260.7 μs. These findings highlight the potential of compound **16** for white light emitting devices. Detection studies with Eu³⁺/Tb³⁺@compound **16** (3:2) (**16d**) confirmed its applicability as a probe for Fe³⁺ and Cr₂O₇^{2−} ions (Table 6, Entry 8).

In a subsequent report, Xian and coworkers described the synthesis and characterization of {[Zn(L)_{0.5}(3-L₁-5-L₂-TZ)]·H₂O·DMF}_n (**17**, Scheme 16), obtained from 3-(4'-(imidazolobenzene)-5-(pyridine-4'-yl)-1,2,4-triazole ([3-L₁-5-L₂-TZ, L₁ = 4-imidazolobenzene, L₂ = 4-pyridyl], **17a**) and 1,3-bis(3,5-dicarboxyphenoxy)benzene (H₄L, **17b**) as ligands [101]. The reaction was carried out using zinc nitrate hexahydrate in an aqueous DMF solution. The luminescent properties of compound **17** (Table 1) were investigated, and its

potential application as a multifunctional sensor was evaluated. Luminescence quenching was observed for nitrofurazone (NZF) (Table 7, Entry 3), Fe^{3+} , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ ions (Table 6, Entry 9) in aqueous solutions. A comparable response was also obtained in the presence of *p*-aminophenol (PAP) (Table 7, Entry 3) in simulated urine, a known biomarker of phenamine, which highlights its significance for medical diagnostics.

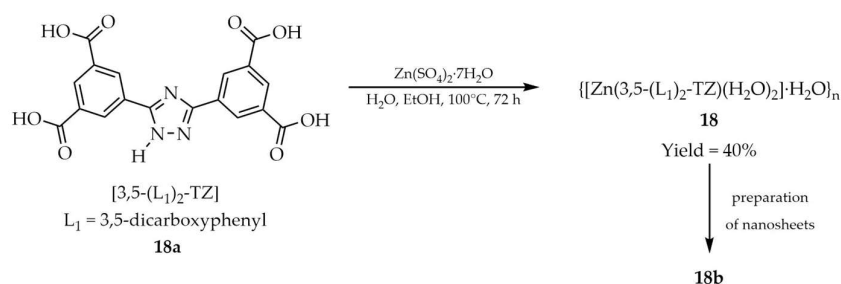


Scheme 15. Preparation of zinc-based frameworks (**16**, **16c**, **16d**) from 4-amino-3,5-bis(4-pyridyl)-1,2,4-triazole (**16a**).



Scheme 16. Synthesis of a Zn-MOF (**17**) using 3-(4'-imidazolobenzene)-5-(pyridine-4'-yl)-1,2,4-triazole (**17a**) and 1,3-bis(3,5-dicarboxyphenoxy)benzene (**17b**).

Yu and coworkers reported the synthesis of two-dimensional (2D) metal-organic framework (MOF) nanosheets via a facile top-down strategy, derived from a three-dimensional (3D) layered MOF $\{[\text{Zn}(3,5\text{-(L}_1\text{)}_2\text{-TZ)}(\text{H}_2\text{O})_2]\cdot \text{H}_2\text{O}\}_n$ (**18**, Scheme 17), and explored their luminescence-based applications (Table 1) [102]. The reaction employed 3,5-bis(3',5'-dicarboxyphenyl)-1*H*-1,2,4-triazole ($[3,5\text{-(L}_1\text{)}_2\text{-TZ}]$, $\text{L}_1 = 3,5\text{-dicarboxyphenyl}$), **18a**) as ligand and zinc salt ($\text{Zn}(\text{SO}_4)_2\cdot 7\text{H}_2\text{O}$) as the metal source, performed in an aqueous ethanol solution. The study focused on the luminescent sensing of selected anti-inflammatory drugs and pesticides. Both the bulk MOF (**18**) and the exfoliated nanosheets (**18b**) were examined, with the latter exhibiting enhanced quenching efficiency due to their larger surface area. A total of eight commercial pharmaceuticals were tested, including anti-inflammatory agents: salicylic acid (SA), naproxen (NP), ibuprofen (BF), and diclofenac sodium (DCF), as well as antibiotics: penicillin (PC), nalidixic acid (NA), neomycin sulfate (NS), and erythromycin (EC). Colloidal suspensions of nanosheets-MOF (**18b**) containing these drugs were probed for luminescence quenching. The strongest response was observed for DCF (93.20%, Table 7, Entry 4), while significantly lower values were recorded for EC, NS, and NA at 24.86%, 22.10%, and 19.78%, respectively. The remaining analytes (SA, NP, BF, and PC) showed negligible quenching effects. In addition, seven pesticides: tebuconazole (TZ), cyanazine (CZ), amitrole (AR), permethrin (PT), atrazine (AZ), diuron (DR), and tetramethylthiuram disulfide (TMTD) were screened. High selectivity was demonstrated towards TMTD, for which luminescence quenching reached 94.79% (Table 7, Entry 4), whereas the other pesticides induced only minor effects.



Scheme 17. Synthesis of a zinc–framework (**18**) from 3,5-bis(3',5'-dicarboxyphenyl)-1H-1,2,4-triazole (**18a**) and the subsequent preparation of nanosheets (**18b**).

In 2024, Chen and coworkers reported the synthesis of a three-dimensional dinuclear zinc-based metal–organic framework $\{[Zn_2 \cdot (3-NH_2-TZ)_2 \cdot (pta)] \cdot 3H_2O\}_n$ (**19**, Scheme 18), constructed from 3-amino-1,2,4-triazole (3-NH₂-TZ), **19a** and terephthalic acid (H₂pta, **19b**), under solvothermal conditions using Zn(NO₃)₂ [103]. A crystalline nanomaterial (**19c**) with particle sizes of ca. 100 nm was prepared by means of a cell fragmentation apparatus and subjected to further analyses. The fluorescence lifetime of **19c** was determined to be 2.7241 ns, with a quantum yield of 3.02%. In addition to its luminescent properties (Table 1), attention was directed toward the capacity of **19c** to adsorb hexavalent chromium. The effects of dosage, pH, and temperature on adsorption efficiency were systematically evaluated. The maximum experimental adsorption capacity of **19c** reached 125.52 mg/g. Reusability studies revealed that, after five adsorption–desorption cycles, the material retained ~98% of its adsorption efficiency.

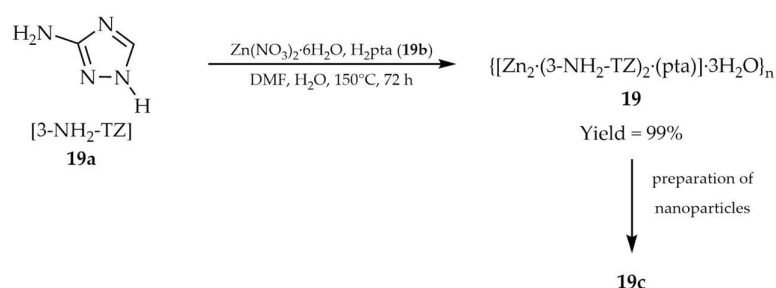
Table 1. Luminescence properties of Zn-MOFs based on 1,2,4-triazole.

Zn-MOFs				
MOF	λ_{abs} [nm]	λ_{ex} [nm]	λ_{em} [nm]	Ref.
5 ^a	-	327	392	[90]
5a ^a	-	350	421	
5b ^a	-	345	394	
6 ^a	~290	270	295	[91]
6a ^a	-	270	274	
7 ^a	-	310	375; 474	
7a ^a	-	290	354	[92]
7b ^a	-	346	563	
8 ^b	420	326	420	[93]
8a ^a	-	380	~482	
9 ^c	310	310	410	
10 ^a	280–340	335	396	[95]
10a ^a	~315	-	-	
11 ^a	280–340	330	384	
4 ^a	-	382	433, 487–600	[52]

Table 1. Cont.

Zn-MOFs				
MOF	λ_{abs} [nm]	λ_{ex} [nm]	λ_{em} [nm]	Ref.
12 ^a	337, 450	280	392	[96]
12b ^a	331, 450	280	389	
13 ^a	-	322 ^a , 302 ^d	408 ^a , 333 ^d	[97]
13a ^a	-	299 ^a , 291 ^d	357 ^a , 333 ^d	
14 ^e	-	340	459	[98]
14a ^e	-	340	366, 423	
14b ^e	-	340	524	
15 ^a	-	328	418	[99]
15a ^a	-	330	410	
16 ^a	-	359 ^a , 290 ^f	415 ^a , 370 ^f	[100]
16a ^a	-	290	354	
16b ^a	-	346	563	
17 ^a	-	335	395	[101]
17a ^a	-	278	429	
17b ^a	-	320	398	
18 ^g	-	285	370	[102]
18a ^g	-	285	348	
18b ^h	-	285	359	
19a ^a	-	340	400	[103]
19b ^a	-	350	430	
19c ^a	-	340	451	

^a solid state; ^b ground sample immersed in 1 mL DMF: H₂O (*v/v* = 1:1); ^c suspension in water; ^d dispersed in DMF; ^e powder; ^f suspension in DMF; ^g indefinite; ^h suspension in MeOH/isopropanol (*v/v* = 4:1).

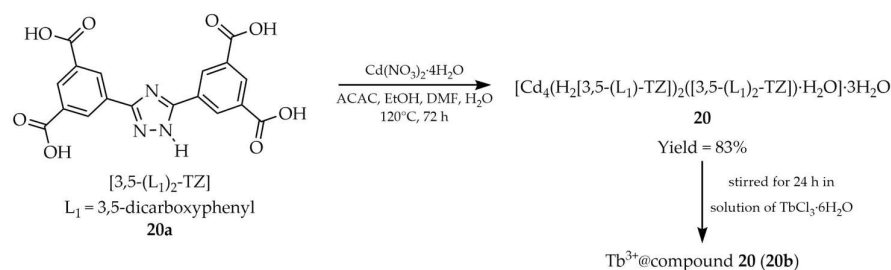


Scheme 18. Synthesis of a zinc-based MOF (**19**) from 3-amino-1,2,4-triazole (**19a**) and terephthalic acid (**19b**) followed by the preparation of nanoparticles (**19c**).

3.1.2. Cadmium-Based Metal–Organic Frameworks Containing 1,2,4-Triazole Linker

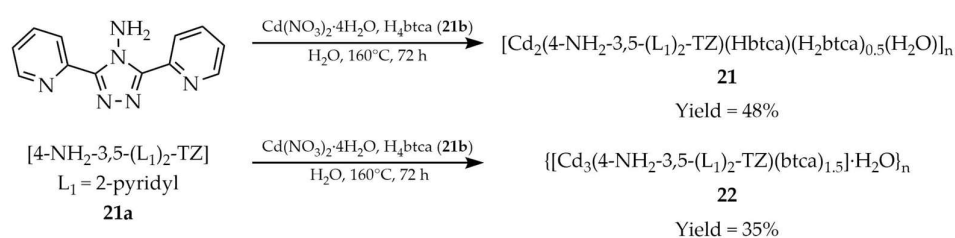
Another frequently employed ion in the synthesis of 1,2,4-triazole-based MOFs is cadmium cation Cd²⁺. In 2019, three research articles addressing this topic were published. Cui et al. reported the solvothermal synthesis of [Cd₄(H₂3,5-(L₁)₂-TZ)₂(3,5-(L₁)-TZ)·H₂O]·3H₂O (**20**, Scheme 19) using 5,5'-(1*H*-1,2,4-triazole-3,5-diyl)diisophthalic acid ([3,5-(L₁)-TZ, L₁ = 3,5-dicarboxyphenyl], **20a**), cadmium nitrate tetrahydrate in a mixed solvent system of acetylacetone (ACAC), ethanol, and DMF [104]. The obtained MOF **20** was post-synthetically functionalized with Tb³⁺ cations, resulting in a new material (**20b**)

exhibiting enhanced luminescent properties (Table 2), characterized by green emission under UV irradiation. Moreover, it proved to be a highly selective and sensitive fluorescent probe for detecting arginine in urine at low concentrations of 0.69 ppm in water (Table 7, Entry 5). Arginine is a biomarker of cystinuria, an autosomal recessive genetic disease that leads to impaired absorption of dibasic amino acids such as cystine, lysine, ornithine, and arginine. Importantly, other components contained in urine had a negligible effect on the degree of luminescence quenching. A paper fluorescence assay was developed by applying compound **20b** to filter paper, demonstrating the application potential of the presented research.



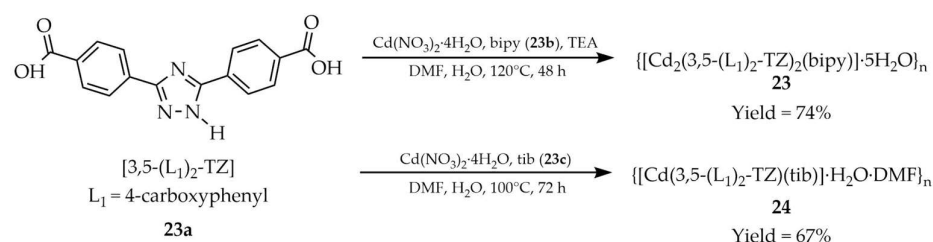
Scheme 19. Synthesis of a cadmium-based MOF (**20**) using 5,5'-(1H-1,2,4-triazole-3,5-diyl)diisophthalic acid (**20a**) and its subsequent modification into a terbium-containing compound.

Another article from 2019 by Zhang et al. described the synthesis and characterization of two cadmium-based luminescent MOFs: [Cd₂(4-NH₂-3,5-(L₁)₂-TZ)(Hbtca)(H₂btca)_{0.5}(H₂O)]_n (**21**, Scheme 20) and {[Cd₃(4-NH₂-3,5-(L₁)₂-TZ)(btca)_{1.5}]·H₂O]_n (**22**, Scheme 20) [105]. The frameworks were constructed using two ligands: 3,5-di(2-pyridyl)-4-amino-1,2,4-triazole ([4-NH₂-3,5-(L₁)₂-TZ, L₁ = 2-pyridyl], **21a**) and 1,2,4,5-benzenetetracarboxylic acid (H₄btca, **21b**), which were used in various molar ratios, and an aqueous solution of Cd(NO₃)₂·4H₂O. Compound **21** exhibited luminescence quenching in the presence of 2,4,6-trinitrophenol (TNP, Table 7, Entry 6 and 7), and a simple paper-based test was devised for detection by immersion in the solution. This is an example of the practical application of the presented research. Quenching was also observed in the presence of Cu²⁺ cation (Table 6, Entry 10).



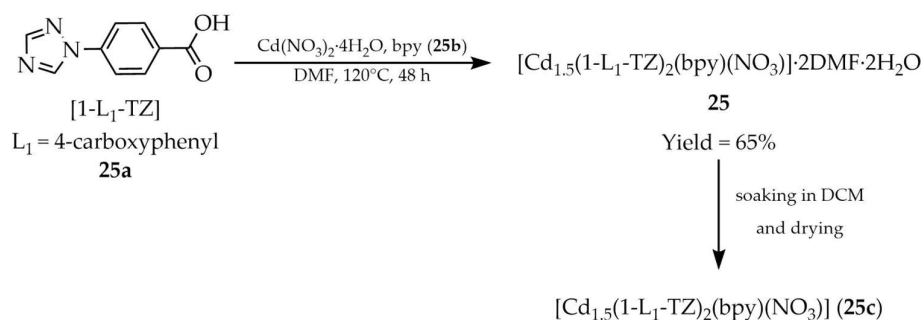
Scheme 20. Preparation of cadmium-based MOFs (**21**, **22**) from 3,5-di(2-pyridyl)-4-amino-1,2,4-triazole (**21a**) and 1,2,4,5-benzenetetracarboxylic acid (**21b**).

Zhang and coworkers reported the synthesis of two cadmium-based MOFs named {[Cd₂(3,5-(L₁)₂-TZ)₂(bipy)]·5H₂O]_n (**23**, Scheme 21) and {[Cd(3,5-(L₁)₂-TZ)(tib)]·H₂O·DMF]_n (**24**) using three ligands: 3,5-bis(4'-carboxyphenyl)-1,2,4-triazole ([3,5-(L₁)₂-TZ, L₁ = 4-carboxyphenyl], (**23a**), 4,4'-bipyridine (bipy, **23b**), and 1,3,5-tris(1-imidazolyl)benzene (tib, **23c**) [106]. Both products **23** and **24** displayed luminescent properties (Table 2). Additionally, compound **24** was tested for solvent detection and showed pronounced luminescence quenching in aqueous acetonitrile solutions (Table 7, Entry 8).



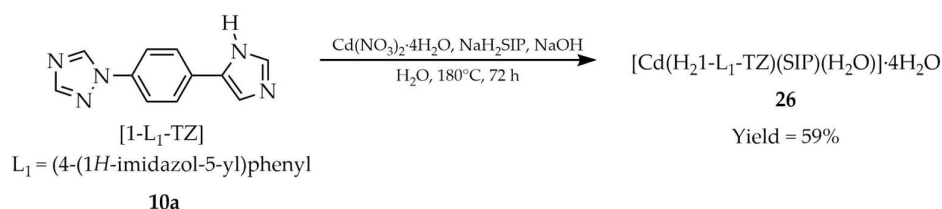
Scheme 21. Synthesis of cadmium-based frameworks (**23**, **24**) from 3,5-bis(4'-carboxyphenyl)-1,2,4-triazole (**23a**), 4,4'-bipyridine (**23b**), and 1,3,5-tris(1-imidazolyl)benzene (**23c**).

In 2020, Singh and co-workers synthesized $[Cd_{1.5}(1-L_1-TZ)_2(bpy)(NO_3)] \cdot 2DMF \cdot 2H_2O$ (**25**, Scheme 22) employing two heterocyclic ligands: 1-(4-carboxyphenyl)-1,2,4-triazole ($[1-L_1-TZ]$, $L_1 = 4\text{-carboxyphenyl}$, **25a**) and 4,4'-bipyridine (bpy, **25b**) [107]. The activated MOF with the formula $[Cd_{1.5}(1-L_1-TZ)_2(bpy)(NO_3)]$ (**25c**) exhibited high CO₂ adsorption selectivity over N₂ and CH₄, rendering it a promising candidate for gas separation applications. Moreover, due to the luminescence quenching phenomenon (Table 6, Entry 11) compound **25c** enables the detection of Fe³⁺ cations and anions containing chromium(VI) (CrO₄²⁻ and Cr₂O₇²⁻).



Scheme 22. Preparation of cadmium-based frameworks (**25**, **26**) employing 1-(4-carboxyphenyl)-1,2,4-triazole (**25a**) and 4,4'-bipyridine (**25b**).

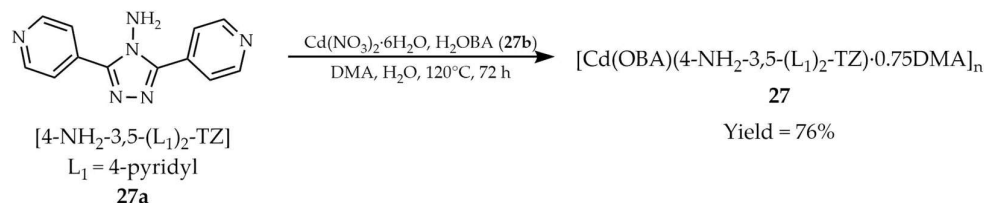
In the previously mentioned work by Li et al., the cadmium-based MOF $[Cd(H_21-L_1-TZ)(SIP)(H_2O)] \cdot 4H_2O$ (**26**, Scheme 23) was synthesized from 1-(4-(1H-imidazole-5-yl)phenyl)-1H-1,2,4-triazole ($[1-L_1-TZ]$, $L_1 = (4\text{-(1H-imidazole-5-yl)phenyl})$, **10a**), sodium 5-sulfoisophthalate (NaH₂SIP), and cadmium salt hydrate in aqueous medium [95]. The luminescent properties of **26** were evaluated (Table 2) and its quantum efficiency was determined to be 2.62%, and the luminescence lifetime was 14.62 ns.



Scheme 23. Synthesis of a cadmium-based MOF (**26**) from 1-(4-(1H-imidazole-5-yl)phenyl)-1H-1,2,4-triazole (**10a**).

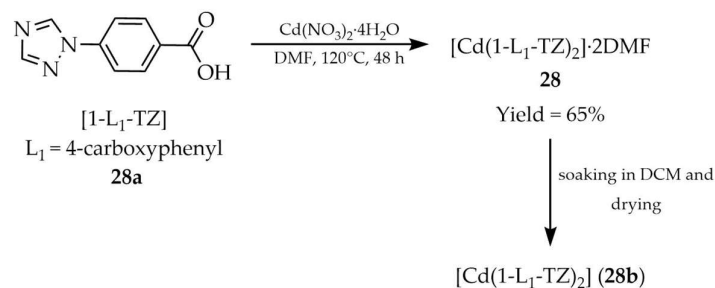
Qin and coworkers reported the solvothermal synthesis of a luminescent material with the formula $[Cd(OBA)(4-NH_2-3,5-(L_1)_2-TZ) \cdot 0.75DMA]_n$ (**27**, Scheme 24), obtained from 4-amino-3,5-bis(4-pyridyl)-1,2,4-triazole ($[4-NH_2-3,5-(L_1)_2-TZ]$, $L_1 = 4\text{-pyridyl}$, **27a**) and 4,4'-oxybis(benzoic acid) (H₂OBA, **27b**) [108]. Upon activation, compound **27** exhibited sorption properties towards H₂ and CO₂. Moreover, it was found to act as a sensitive and selective

sensor for Cr^{3+} , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ ions (Table 6, Entry 12). A luminescent response was also obtained for a paper test prepared by the researchers, which was obtained by applying substance **27** to the blotting paper, highlighting the potential practical application of these studies.



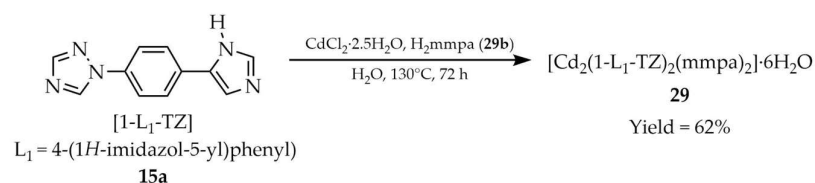
Scheme 24. Formation of a cadmium-based framework (**27**) from 4-amino-3,5-bis(4-pyridyl)-1,2,4-triazole (**27a**) and 4,4'-oxybis(benzoic acid) (**27b**).

In 2021, Singh and coworkers described the synthesis of a MOF with the formula $[\text{Cd}(1\text{-L}_1\text{-TZ})_2] \cdot 2\text{DMF}$ (**28**, Scheme 25), prepared from 4-(1,2,4-triazol-1-yl)benzoic acid ($[1\text{-L}_1\text{-TZ}]$, $\text{L}_1 = 4\text{-carboxyphenyl}$, **28a**), cadmium salt such as $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and DMF as a solvent [109]. The material was activated by removal of DMF molecules from the framework (**28b**), and its sorption capacity revealed CO_2 uptake at 298K of $29.23 \text{ cm}^3 \text{ g}^{-1}$ (1.30 mmol g^{-1}). Furthermore, high selectivity for CO_2 over N_2 and CH_4 was demonstrated. Compound **28b** was also shown to act as a luminescent sensor exhibiting a “turn-on” luminescence response for the detection of toxic compounds such as 3-(diethylamino)phenol (DEP) and the pesticide isoproturon (IPT) (Table 7, Entry 9). In addition, a “turn-off” luminescence response was observed for the detection of the pesticide dichloran (2,6-dichloro-4-nitroaniline) (Table 7, Entry 9) with high selectivity and a very low detection limit (124 nM), accompanied by distinct colorimetric changes under UV light.



Scheme 25. Synthesis of a cadmium-based framework (**28**) using 4-(1,2,4-triazol-1-yl)benzoic acid (**28a**) and its subsequent modification into **28b**.

Chen and coworkers reported the synthesis of a MOF with the formula $[\text{Cd}_2(1\text{-L}_1\text{-TZ})_2(\text{mmpa})_2] \cdot 6\text{H}_2\text{O}$ (**29**, Scheme 26), obtained from 1-(4-(1*H*-imidazol-5-yl)phenyl)-1*H*-1,2,4-triazole ($[1\text{-L}_1\text{-TZ}]$, $\text{L}_1 = (4\text{-}1\text{H-imidazol-5-yl)phenyl}$), **15a**) and 5-methylisophthalic acid (H_2mmpa , **29b**) [99]. The luminescent properties of compound **29** were studied (Table 2), revealing a luminescence lifetime of 16 ns and a quantum yield of ~5% (5.32%). Through luminescence quenching, compound **29** was able to detect 4-nitrophenol (NP) (Table 7, Entry 10) and Ag^+ cations (Table 6, Entry 13). Sorption tests revealed that the microporous material **29** exhibited selective adsorption of CO_2 over N_2 , as well as water vapor uptake.



Scheme 26. Preparation of a Cd-based MOF (**29**) from 1-(4-(1*H*-imidazol-5-yl)phenyl)-1*H*-1,2,4-triazole (**15a**) and 5-methylisophthalic acid (**29b**).

In 2022, Hong et al. published a study describing the solvothermal synthesis of two luminescent MOFs: $\{[Cd(\mu_2-CN)_{0.5}(1,4-BDC)(H_2O)]_2(4-L_1-TZ)\} \cdot 2H_2O$ (**30**, Scheme 27) and $[Cd_2(1,4-BDC)_2(H_2O)_2]_2(4-L_1-TZ)$ (**31**) [110]. For their preparation, two ligands were used: 1,4-phenylene-4,4'-bis(1,2,4-triazole) ($[4-L_1-TZ]$, $L_1 = 4-(1,2,4-triazol-4-yl)phenyl$], **30a**), 1,4-dicarboxybenzene (1,4- H_2BDC , **30b**) and cadmium sulfate. The same reagents were employed for both syntheses, with the difference being that a solvent mixture of DMF/ CH_3CN/H_2O ($v/v/v$; 1:3:2) was used for compound **30**, while for compound **31** the ratio was 1:4:1, respectively. Luminescence studies were also performed (Table 2). Interestingly, for compound **30** the emission intensity decreased with increasing temperature, whereas for compound **31** the emission intensity initially increased with temperature between 80 and 130 K, but decreased at temperatures above 130 K. Good linearity and reversibility were demonstrated for these responses, indicating the potential of the obtained materials as thermometric sensors.

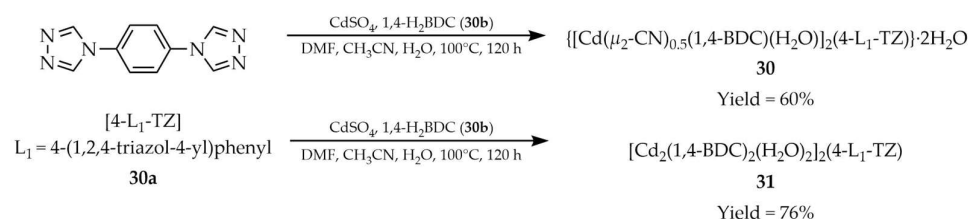
Table 2. Luminescence properties of Cd-MOFs based on 1,2,4-triazole.

Cd-MOFs				
MOF	λ_{abs} [nm]	λ_{ex} [nm]	λ_{em} [nm]	Ref.
20 ^a	-	323	458	[104]
20a ^a	-	323	470	
20b ^a	-	285	490, 546, 585, 620	
21 ^a	-	357	427	[105]
21a ^a	-	357	404	
22 ^a	-	357	420	
23 ^a	-	425	369	[106]
23a ^a	-	273	376	
23b ^a	-	344	415	
23c ^a	-	360	407	[107]
24 ^a	-	450	368	
25c ^b	-	265	406	
26 ^a	280–340	336	428	[95]
10a ^a	315	-	-	
27 ^a	-	368	420	
27a ^a	-	290	354	[108]
27b ^a	-	346	563	

Table 2. Cont.

Cd-MOFs				
MOF	λ_{abs} [nm]	λ_{ex} [nm]	λ_{em} [nm]	Ref.
28b ^c	-	272	329	[109]
29 ^a	-	323	375	
15a ^a	-	330	410	[99]
29b ^a	-	280	~380	
30 ^a	-	330	428	[110]
30a ^a	-	330	440	
31 ^a	-	330	434	

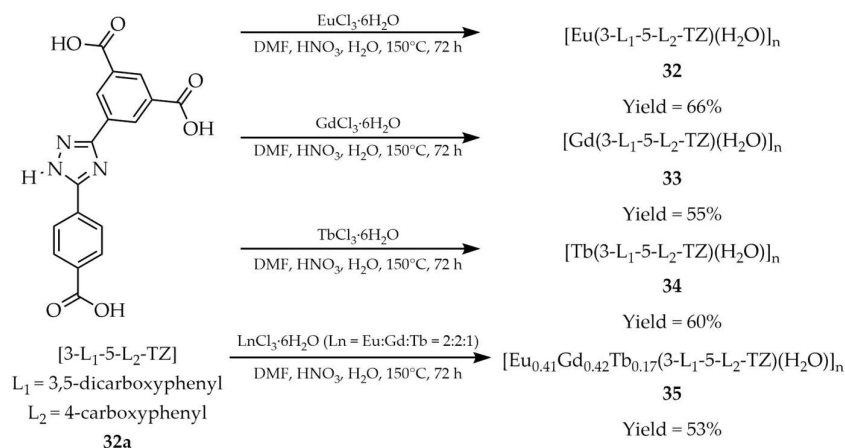
^a solid state; ^b suspension in water; ^c suspension in DMF.



Scheme 27. Synthesis of cadmium-based frameworks (**30**, **31**) starting from 1,4-phenylene-4,4'-bis(1,2,4-triazole) (**30a**) and 1,4-dicarboxybenzene (**30b**).

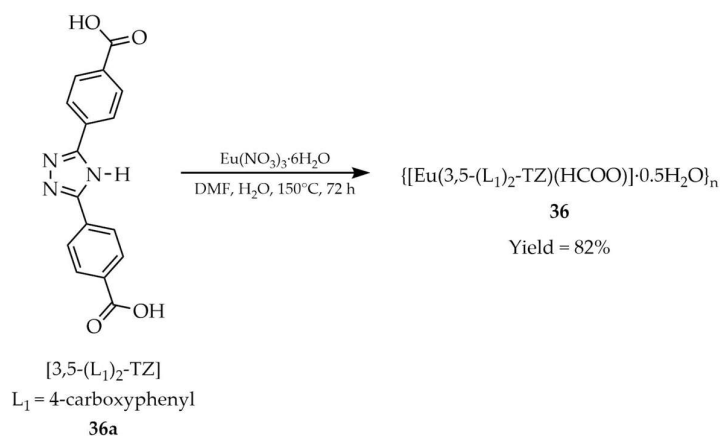
3.1.3. Lanthanide-Based Metal–Organic Frameworks Containing 1,2,4-Triazole Linker

From the lanthanide family, MOFs in which 1,2,4-triazole was coordinated with europium, gadolinium, terbium, lanthanum, holmium, and dysprosium have been primarily investigated. In 2019, Yu and coworkers reported the synthesis of four lanthanide derivatives: [Eu(3-L₁-5-L₂-TZ)(H₂O)]_n (**32**, Scheme 28), [Gd(3-L₁-5-L₂-TZ)(H₂O)]_n (**33**), [Tb(3-L₁-5-L₂-TZ)(H₂O)]_n (**34**) and [Eu_{0.41}Gd_{0.42}Tb_{0.17}(3-L₁-5-L₂-TZ)(H₂O)]_n (**35**), obtained using the ligand (3-(3,5-dicarboxylphenyl)-5-(4-carboxylphenyl)-1*H*-1,2,4-triazole ([3-L₁-5-L₂-TZ, L₁ = 3,5-dicarboxyphenyl, L₂ = 4-carboxyphenyl], **32a**) [111]. The reactions were carried out with hydrated salts EuCl₃·6H₂O, GdCl₃·6H₂O, and TbCl₃·6H₂O in a mixture of DMF, water, and HNO₃. One of the products, **35**, containing europium, gadolinium, and terbium, exhibited white-light emission with CIE coordinates (0.330, 0.338) upon excitation at 320 nm, both in the solid state and in a well-dispersed 0.01 M aqueous suspension. Its sensing properties toward twenty selected antibiotics from six classes were studied, including β-lactams: penicillin (PCL), amoxicillin (ACL), cefixime (CFX), cefradine (CFD); aminoglycosides: gentamycin (GTM), kanamycin (KNM); macrolides: roxithromycin (ROX), azithromycin (AZM); quinolones: ciprofloxacin (CPFX), norfloxacin (NFX); nitrofurans: nitrofurazone (NZF), nitrofurantoin (NFT); nitroimidazoles: metronidazole (MNZ), dimetridazole (DTZ), ornidazole (ODZ); and others: tetracycline hydrochloride (TC), vancomycin (VCC), sulfadiazine (SDZ), lincomycin (LCC), and carbamazepine (CBZ) in aqueous solution. Eight compounds provided a selective luminescence response (Table 7, Entry 11). A color change in the luminescence was observed upon addition of tetracycline hydrochloride (TC) and nitrofurans (NZF and NFT), shifting to yellow and orange, respectively. For sulfadiazine (SDZ) and carbamazepine (CBZ), a blue shift was noted, while nitroimidazole antibiotics (MNZ, DTZ, and ODZ) induced pronounced luminescence quenching.



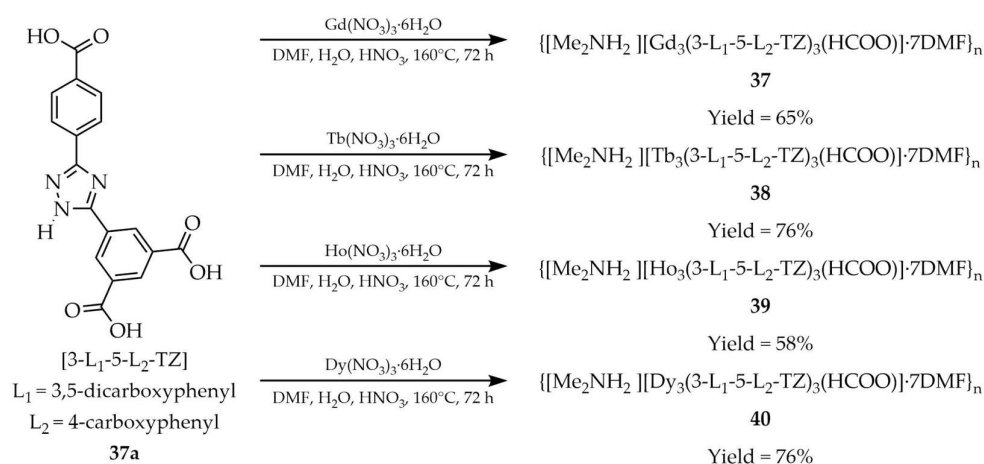
Scheme 28. Synthesis of four MOFs (**32**, **33**, **34**, **35**) from (3-(3,5-dicarboxyphenyl)-5-(4-carboxyphenyl)-1*H*-1,2,4-triazole (**32a**) and hexahydrate lanthanide chlorides.

Li and coworkers reported the synthesis of a metal–organic framework $\{[\text{Eu}(3,5-(L_1)_2\text{-TZ})(\text{HCOO})] \cdot 0.5\text{H}_2\text{O}\}_n$ (**36**, Scheme 29), obtained from europium salt $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ under solvothermal conditions using the ligand 3,5-bis(4'-carboxyphenyl)-1,2,4-triazole ($[3,5-(L_1)_2\text{-TZ}]$, $L_1 = 4\text{-carboxyphenyl}$), **36a**) [112]. Studies demonstrated that this compound could serve as a luminescent sensor for the detection of PO_4^{3-} anion (Table 6, Entry 14) and acetylacetone (Table 7, Entry 12) in aqueous solution.



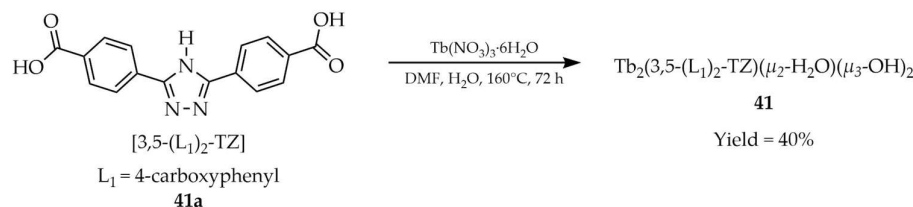
Scheme 29. Preparation of a europium-based MOF (**36**) using 3,5-bis(4'-carboxyphenyl)-1,2,4-triazole (**36a**).

In 2021, Zhan and coworkers described the synthesis of four MOFs: $\{[\text{Me}_2\text{NH}_2][\text{Ln}_3(3-L_1-5-L_2\text{-TZ})_3(\text{HCOO})] \cdot 7\text{DMF}\}_n$ ($\text{Ln} = \text{Gd}$ (**37**), $\text{Ln} = \text{Tb}$ (**38**), $\text{Ln} = \text{Ho}$ (**39**), $\text{Ln} = \text{Dy}$ (**40**) Scheme 30), obtained from solvothermal reactions of the hydrated nitrates of gadolinium, terbium, holmium, and dysprosium with the tricarboxylate ligand 3-(3,5-dicarboxyphenyl)-5-(4-carboxyphenyl)-1,2,4-triazole ($[3-L_1-5-L_2\text{-TZ}]$, $L_1 = 3,5\text{-dicarboxyphenyl}$, $L_2 = 4\text{-carboxyphenyl}$), **37a**) [113]. The luminescence properties of compound **38** (Table 3) were investigated and demonstrated potential for the detection of nitroaromatic compounds through luminescence quenching. Compound **37** containing Gd(III), after desolvation, exhibited high selectivity for adsorption of C_2H_2 and CO_2 over CH_4 , indicating potential for use in industrial gas separation.



Scheme 30. Synthesis of lanthanide-based MOFs (**37**, **38**, **39**, **40**) from 3-(3,5-dicarboxylphenyl)-5-(4-carboxylphenyl)-1,2,4-triazole (**37a**).

The Zhang group reported one metal–organic framework based on terbium(III) with the formula $\text{Tb}_2(3,5\text{-(L}_1)_2\text{-TZ})(\mu_2\text{-H}_2\text{O})(\mu_3\text{-OH})_2$ (**41**, Scheme 31), synthesized from the dicarboxylate ligand 3,5-bis(4'-carboxyphenyl)-1,2,4-triazole ([3,5-(L₁)₂-TZ, L₁ = 4-carboxyphenyl], **41a**), hydrated terbium nitrate, and a water–DMF solvent mixture [114]. The product exhibited stability in various organic solvents as well as in aqueous media over a wide pH range (0–11). Luminescence studies revealed that compound **41** selectively quenched luminescence in the presence of MnO_4^- ions (Table 6, Entry 15) and could also detect aromatic nitro-compounds in DMF solution, particularly 4-nitrophenol (Table 7, Entry 13). Its quantum yield was estimated at 9.5%, with a luminescence lifetime of 143 μs observed at the emission wavelength of 548 nm.

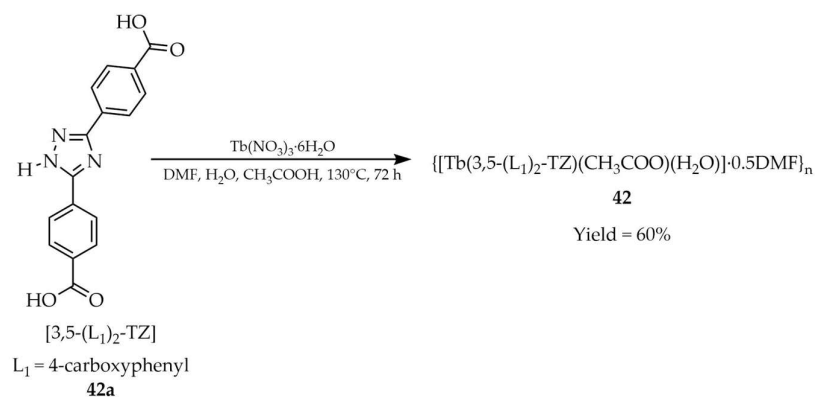


Scheme 31. Formation of a terbium-based framework (**41**) from 3,5-bis(4'-carboxyphenyl)-1,2,4-triazole (**41a**).

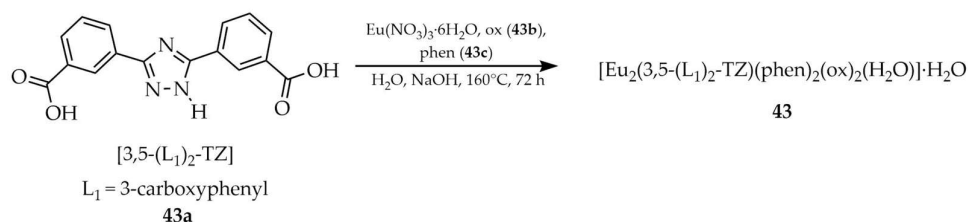
In 2022, Luo and coworkers presented the synthesis of $\{[\text{Tb}(3,5\text{-(L}_1)_2\text{-TZ})(\text{CH}_3\text{COO})(\text{H}_2\text{O})] \cdot 0.5\text{DMF}\}_n$ (**42**, Scheme 32) using 3,5-bis(4'-carboxyphenyl)-1,2,4-triazole ([3,5-(L₁)₂-TZ, L₁ = 4-carboxyphenyl], **42a**) as an organic ligand with the participation of $\text{Tb(NO}_3)_3 \cdot 6\text{H}_2\text{O}$ [115]. The reaction was conducted in a three-component solvent mixture of water, DMF, and acetic acid. Product **42** functioned as a luminescent sensor for creatinine detection in aqueous solution (Table 7, Entry 14), an important biomarker in medical diagnostics with key relevance for kidney function monitoring. Moreover, the sensor retained its activity in diluted serum samples and could be recycled and reused at least five times without significant loss of sensitivity.

Wang and coworkers described the synthesis of MOFs based on the salt: hydrated europium(III) nitrate and ligands: 3,5-bis(3'-carboxyphenyl)-1,2,4-triazole ([3,5-(L₁)₂-TZ, L₁ = 3-carboxyphenyl], **43a**, Scheme 33), oxalate (ox, **43b**) and 1,10-phenanthroline (phen, **43c**) [116]. The obtained compound, $[\text{Eu}_2(3,5\text{-(L}_1)_2\text{-TZ})(\text{phen})_2(\text{ox})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (**43**), exhibited a quantum yield of 52.51%. It demonstrated a highly selective luminescence quenching response to colchicine (Table 7, Entry 15), even in the presence of interfering substances. Colchicine is used clinically in the treatment of inflammatory diseases, gout, and cancers.

As a water-soluble compound, its presence in wastewater may exert long-term environmental impacts. In this study, a composite film was fabricated by embedding compound **43** in polytetrafluoroethylene, which exhibited red luminescence that was immediately quenched upon exposure to colchicine.

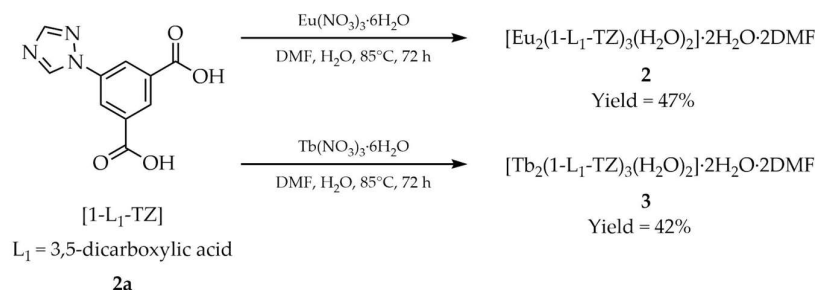


Scheme 32. Synthesis of a terbium-based MOF (**42**) using 3,5-bis(4'-carboxyphenyl)-1,2,4-triazole (**42a**).



Scheme 33. Preparation of a europium-based framework (**43**) from 3,5-bis(3'-carboxyphenyl)-1,2,4-triazole (**43a**), oxalate (**43b**) and 1,10-phenanthroline (**43c**).

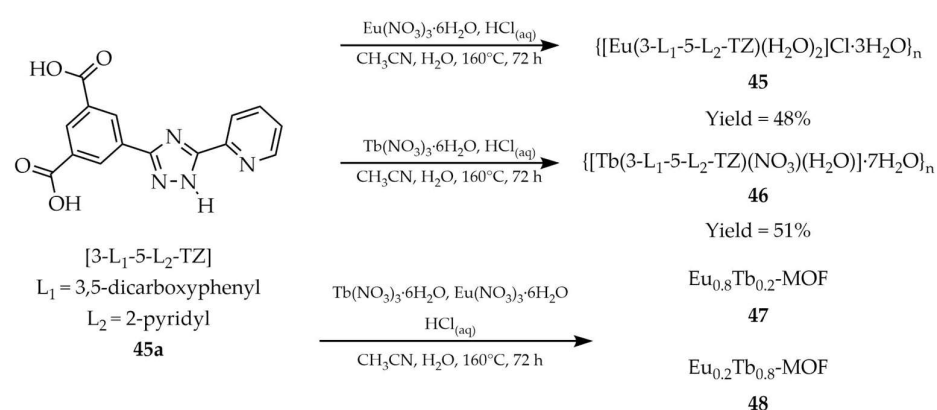
In 2023, Sun and coworkers reported the synthesis of two MOFs with the formula $[\text{Ln}_2(1\text{-}L_1\text{-TZ})_3(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O} \cdot 2\text{DMF}$ containing europium(III) (**2**, Scheme 34) or terbium(III) (**3**) in place of the lanthanide (Ln), and the ligand function was performed by 5-(1*H*-1,2,4-triazol-1-yl)isophthalic acid [$1\text{-}L_1\text{-TZ}$, $L_1 = 3,5\text{-dicarboxylic acid}$], **2a**. The reactions were carried out using hydrated europium and terbium nitrates in a DMF/water solvent mixture. Compound **2** exhibited red emission, while compound **3** displayed green emission. Both materials demonstrated the ability to detect nitroaromatic compounds (NACs) (Table 7, Entry 16 and 17) as well as Fe^{3+} cations (Table 6, Entry 16 and 17).



Scheme 34. Synthesis of lanthanide-based MOFs (**2**, **3**) from 5-(1*H*-1,2,4-triazol-1-yl)isophthalic acid (**2a**).

In a 2024 an article by Wang and coworkers, described the synthesis of a series of metal–organic frameworks based on europium(III) and terbium(III) [117]. Among them, the best bimetallic material, $\text{Eu}_{0.096}\text{Tb}_{0.904}\text{-MOF}$ (**44**, Scheme 35), was identified. This

compound was obtained from europium and terbium chlorides with a dicarboxylate ligand bearing a 1,2,4-triazole ring, namely 5-(4-(triazol-1-yl)phenyl)isophthalic acid ([1-L₁-TZ, L₁ = [(1,1'-biphenyl)-3,5-dicarboxylic acid], **44a**), under DMF/water conditions. The resulting product **44** exhibited the highest quantum yield of 42%, with a luminescence lifetime of 544 μ s. It was shown to act as a detector for hydroxyflutamide, a drug used in the treatment of castration-resistant prostate cancer (CRPC) (Table 7, Entry 18). Excessive use of this drug can lead to serious side effects, which may be mitigated by monitoring its blood concentration. The studies revealed a linear correlation between hydroxyflutamide concentration in human serum and the luminescence response of compound **44**, indicating its potential as a ratiometric luminescent sensor. In a subsequent step, hydroxyflutamide was incorporated into this material (**44b**) to form a composite platform capable of detecting CRPC biomarkers such as the androgen receptor (AR) and prostate-specific antigen (PSA) (Table 7, Entry 19).

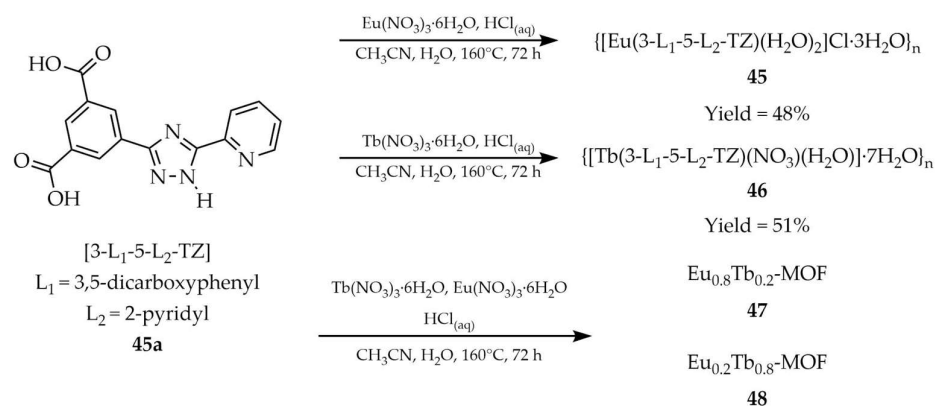


Scheme 35. Preparation of bimetallic europium–terbium-based frameworks (**44**, **44b**) employing 5-(4-(triazol-1-yl)phenyl)isophthalic acid (**44a**).

In 2025, lanthanide-based derivatives functioning as both thermometers and luminescent sensors were described. Zhang and coworkers reported two isostructural MOFs with the formulas $\{[Eu(3-L_1-5-L_2-TZ)(H_2O)_2]Cl \cdot 3H_2O\}_n$ (**45**, Scheme 36) and $\{[Tb(3-L_1-5-L_2-TZ)(NO_3)(H_2O)] \cdot 7H_2O\}_n$ (**46**) [118]. The syntheses employed 3-(3,5-dicarboxyphenyl)-5-(pyrid-2-yl)-1H-1,2,4-triazole ([3-L₁-5-L₂-TZ, L₁ = 3,5-dicarboxyphenyl, L₂ = 2-pyridyl], **45a** as the ligand, hydrated europium and terbium nitrates, and a mixed acetonitrile/water solvent system. The quantum yields of compounds **45** and **46** were determined to be 9.8% and 10.1%, respectively, with corresponding luminescence lifetimes of 1.15 ms and 0.94 ms. Both compounds showed luminescent sensing capability toward Fe³⁺ cations, Cr₂O₇^{2−} anions (Table 6, Entry 18 and 19), and 2,4,6-trinitrophenol (TNP) (Table 7, Entry 20 and 21). In addition, a series of Eu_xTb_{1−x}-MOF was obtained by tuning the molar ratio of Eu³⁺ and Tb³⁺ ions. Among them, Eu_{0.8}Tb_{0.2}-MOF (**47**) emitted nearly ideal white light with CIE coordinates (0.316, 0.332), making it a promising candidate for diode applications. Conversely, Eu_{0.2}Tb_{0.8}-MOF (**48**) exhibited temperature sensitivity, giving a linear luminescent response in the range of 303–373 K.

Li et al. reported the synthesis of $[Eu_3(3,5-(TZ)_2-3',5'-(L_1)_2-1,1'-biphenyl)_4(CH_3COO)(H_2O)_7] \cdot (CH_3CN)_5$ (**49**, Scheme 37), employing (3',5'-di(1H-1,2,4-triazole-1-yl)-[1,1'-biphenyl]-3,5-dicarboxylic acid ([3,5-(TZ)₂-3',5'-(L₁)₂-1,1'-biphenyl, L₁ = carboxyl], **49a**) as the ligand, europium nitrate hexahydrate, and an acetonitrile/water solvent mixture [119]. This compound exhibited a luminescence “turn-off” response in the presence of caffeic acid (CA) (Table 7, Entry 22). While CA exerts beneficial biological effects such as antioxidant and anti-inflammatory activity at low concentrations, at higher levels it may contribute to

carcinogenesis. Therefore, developing methodologies for the determination of its concentration is significant.

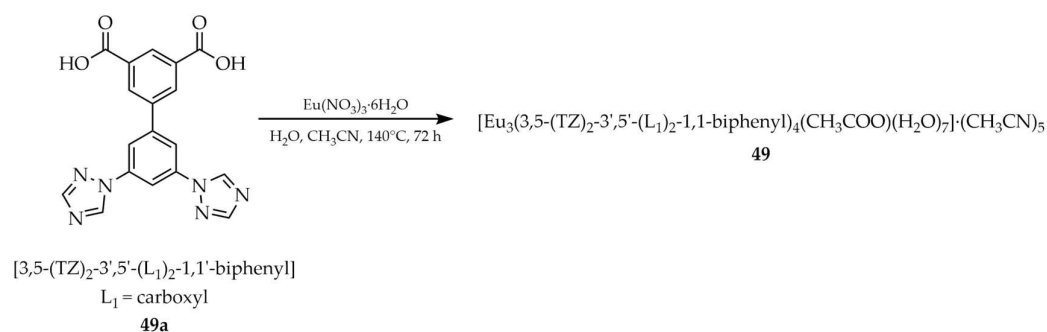


Scheme 36. Synthesis of lanthanide-based MOFs (**45**, **46**, **47**, **48**) using 3-(3,5-dicarboxyphenyl)-5-(pyrid-2-yl)-1H-1,2,4-triazole (**45a**).

Table 3. Luminescence properties of lanthanide metal–organic frameworks based on 1,2,4-triazole.

Ln-MOFs				
MOF	λ_{abs} [nm]	λ_{ex} [nm]	λ_{em} [nm]	Ref.
32	204 ^b	350 ^a	485, 591, 614, 651, 699 ^a	[111]
33	204 ^b	390 ^a	479 ^a	
34	204 ^b	347	491, 545, 584, 619 ^a	
35	204 ^b	320 ^a	439, 490, 545, 590, 613 ^a	
32a	-	372 ^a	420–550 ^a	
36	-	-	594, 617, 652, 699 ^c	[112]
38^a	-	314	543, 584, 621	[113]
37a^a	-	351	408, 468, 520	
41^a	-	280	493, 548, 589, 623	[114]
42^a	-	250	491, 547, 586, 623	[115]
42^c	-	250	380, 491, 547, 586, 623	
42a^c	-	250	~380	
43^a	-	622	336, 395, 466, 536	[116]
43^a	-	336	583, 597, 622, 655, 698	
2^a	-	350	593, 613, 651, 701	[51]
3^a	-	350	489, 545, 588, 621	
44^c	-	250	~350, 492, 543, 583, 617	[117]
45^a	-	300	580, 593, 617, 651, 700	[118]
46^a	-	337	490, 545, 584, 622	
45a^a	-	280	460	
49^a	-	327	589, 614, 648, 696	[119]
49a^a	-	321	350	

^a solid state; ^b in methanol; ^c suspension in water.

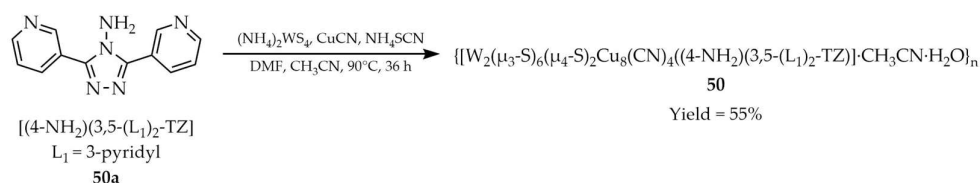


Scheme 37. Synthesis of a europium-based framework (49) from (3',5'-di(1H-1,2,4-triazole-1-yl)-[1,1'-biphenyl]-3,5-dicarboxylic acid (49a).

3.1.4. Cluster-Based Metal–Organic Frameworks Containing 1,2,4-Triazole Linker

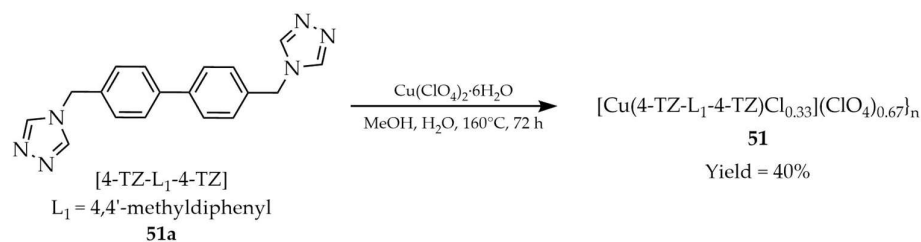
Metal clusters represent a distinct field of inorganic and organometallic chemistry, significantly expanding the diversity of metal–organic frameworks (MOFs) due to their unique architectures. They are defined as molecular compounds containing two or more metal atoms connected by metal–metal bonds or by bridging ligands without direct metal–metal bonding [120].

In 2019, an article of Zhang et al. reported a metal–organic framework based on the heterothiometallic cluster $[\text{W}_2(\mu_3\text{-S})_6(\mu_4\text{-S})_2\text{Cu}_8]^{4+}$ and 4-amino-3,5-bis(3-pyridyl)-1,2,4-triazole ($[(4\text{-NH}_2)(3,5-(\text{L}_1)_2\text{-TZ})]$, $\text{L}_1 = 3\text{-pyridyl}$), 50a, Scheme 38) with the formula $\{[\text{W}_2(\mu_3\text{-S})_6(\mu_4\text{-S})_2\text{Cu}_8(\text{CN})_4((4\text{-NH}_2)(3,5-(\text{L}_1)_2\text{-TZ})] \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}\}_n$ (50) [121]. For the synthesis, in addition to the indicated ligand, $(\text{NH}_4)_2\text{WS}_4$, CuCN and NH_4SCN were used along with DMF and acetonitrile as solvents. Compound 50 exhibited luminescence quenching in the presence of nitroaromatic compounds (NACs): nitrobenzene (NB), 2,4-dinitrotoluene (2,4-DNT), trinitrotoluene (TNT), and trinitrophenol (TNP) in acetonitrile (Table 7, Entry 23). The best detection results were obtained for TNP, which is a contaminant found in aquatic environments; therefore, tests with compound 50 as a suspension in water were also conducted, giving low detection limits ($0.66 \mu\text{M}$).



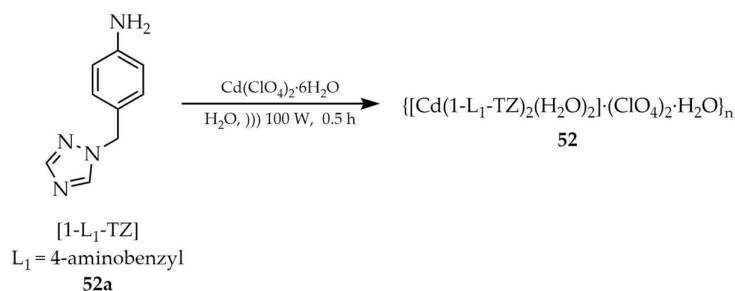
Scheme 38. Preparation of a bimetallic tungsten–copper framework (50) from 4-amino-3,5-bis(3-pyridyl)-1,2,4-triazole (50a).

In 2021, Wang and coworkers described the synthesis of a three-dimensional metal–organic framework $[\text{Cu}(4\text{-TZ-L}_1\text{-4-TZ})\text{Cl}_{0.33}](\text{ClO}_4)_{0.67}]_n$ (51, Scheme 39) constructed from copper clusters and 4,4'-di(4H-1,2,4-triazol-4-yl)methyldiphenyl ($[4\text{-TZ-L}_1\text{-4-TZ}]$, $\text{L}_1 = 4,4'\text{-methyldiphenyl}$), 51a [122]. For the synthesis, $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was used as the metal source and a water/methanol solvent mixture. Luminescence studies of the triazole ligand and compound 51 were performed in DMF and in the solid state (Table 4). The obtained MOF 51 showed a quantum yield of 4.81% and a luminescence lifetime of 1.46 ns. Furthermore, its potential for detection of Dy^{3+} cations, through luminescence enhancement, and CN^- anions, through luminescence quenching, was demonstrated; however, no data on detection limits or enhancement/quenching constants were provided.



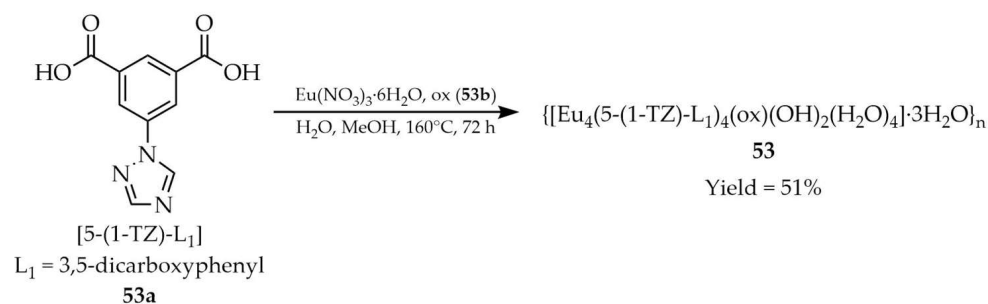
Scheme 39. Synthesis of a copper-based MOF (51) using 4,4'-di(4H-1,2,4-triazol-4-yl)methyldiphenyl (51a).

In the same year, An and coworkers reported the metal–organic framework of the following formula $[\text{Cd}(\text{1-L}_1\text{-TZ})_2(\text{H}_2\text{O})_2] \cdot (\text{ClO}_4)_2 \cdot \text{H}_2\text{O}]_n$ (52, Scheme 40), obtained by a sonochemical method from cadmium(II) clusters and 1-(4-aminobenzyl)-1H-1,2,4-triazole ([1-L₁-TZ, L₁ = 4-aminobenzyl], 52a) [123]. The synthesis was performed using Cd(ClO₄)₂·6H₂O in aqueous solution. Optimal results were achieved with a 1:2 ratio of salt to ligand, an ultrasonic power of 100 W, and a reaction time of 30 min. Compound 52 exhibited good chemical stability in various solvents and aqueous solutions across a wide pH range (2–12). Luminescence studies (Table 7, Entry 24) revealed a luminescence “turn-on” effect in the presence of 5-hydroxytryptamine (5-HT), also known as serotonin. Serotonin is an important neurotransmitter in the human body responsible for regulating many physiological processes such as body temperature, sleep, and appetite. Further luminescence studies of compound 52 (Table 7, Entry 24) showed luminescence quenching in the presence of 2,6-pyridinedicarboxylic acid (DPA), enabling its use as a sensor for this analyte. DPA is a known chelating agent capable of forming coordination compounds with metals.



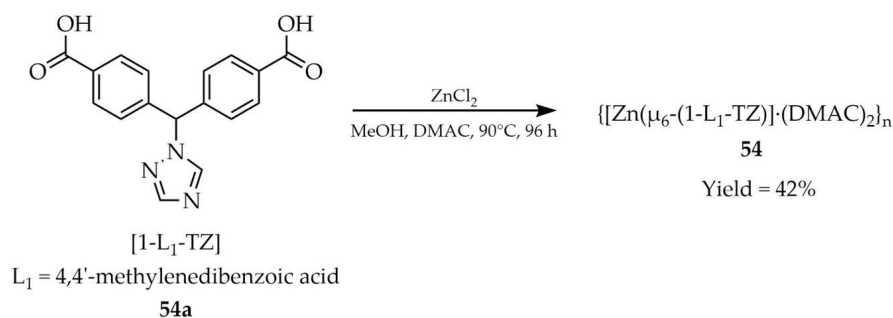
Scheme 40. Formation of 52 from 1-(4-aminobenzyl)-1H-1,2,4-triazole (52a) and cadmium(II) clusters.

Wang and coworkers described the synthesis and characterization of a three-dimensional europium-based MOF. The material $[\text{Eu}_4(5-(1\text{-TZ})\text{-L}_1)_4(\text{ox})(\text{OH})_2(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}]_n$ (53, Scheme 41) was obtained under solvothermal conditions using 5-(1,2,4-triazol-1-yl)isophthalic acid ([5-(1-TZ)-L₁, L₁ = 3,5-dicarboxyphenyl], 53a), oxalic acid (H₂ox, 53b), europium salt Eu(NO₃)₃·6H₂O, and a methanol/water solvent mixture [124]. Compound 53, containing basic triazole Lewis centers, exhibited luminescence (Table 4), which was quenched in the presence of organic amines (Table 7, Entry 25), such as diethylamine (DEA), trimethylamine (TMA), triethylamine (TEA), ethylenediamine (EDA), and aniline. The luminescence quenching mechanism was attributed to differences in the lowest unoccupied molecular orbital (LUMO) energies between the triazole ligand and the tested amines, which hinder energy transfer to the emissive Eu³⁺ state. These findings suggest the potential use of this MOF as a sensor for organic amines, relevant for environmental protection and human health.



Scheme 41. Synthesis of a europium-based MOF (**53**) employing 5-(1,2,4-triazol-1-yl) isophthalic acid (**53a**) and oxalic acid (**53b**).

In the same year, Wang and coworkers presented the structure and properties of a nanoporous zinc-containing MOF $\{[\text{Zn}(\mu_6\text{-(1-L}_1\text{-TZ)}]\cdot(\text{DMAC})_2\}_n$ (**54**, Scheme 42) (DMAC = dimethylacetamide), synthesized from 4,4'-((1*H*-1,2,4-triazol-1-yl)methylene) dibenzoic acid ($[\text{1-L}_1\text{-TZ}]$, $\text{L}_1 = 4,4'\text{-methylenedibenzoic acid}$, **54a**) [125]. The transformation was carried out using ZnCl_2 and methanol and dimethylacetamide as solvents. The developed material **54** could be applied as a luminescent probe for dichromate anions ($\text{Cr}_2\text{O}_7^{2-}$) (Table 6, Entry 20), showing a correlated luminescence quenching response. Furthermore, compound **54** was sensitive to dipicolinic acid (DPA) (Table 7, Entry 26), characteristic of anthrax spores, which may occur in raw milk, making it a useful luminescent probe for their detection. However, the authors did not provide detailed luminescence data for compound **54**.



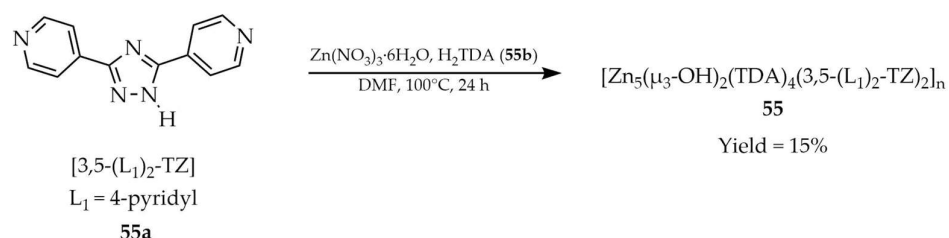
Scheme 42. Preparation of a nanoporous zinc-based MOF (**54**) from 4,4'-((1*H*-1,2,4-triazol-1-yl)methylene)dibenzoic acid (**54a**).

In 2022, Liu and coworkers investigated a luminescent MOF based on a $\{\text{Zn}_5\}$ cluster with the formula $[\text{Zn}_5(\mu_3\text{-OH})_2(\text{TDA})_4(3,5\text{-(L}_1\text{)}_2\text{-TZ)}_2]_n$ (**55**, Scheme 43), constructed from 1*H*-3,5-bis(4-pyridyl)-1,2,4-triazole ($[\text{3,5-(L}_1\text{)}_2\text{-TZ}]$, $\text{L}_1 = 4\text{-pyridyl}$, **55a**) and thiophene-2,5-dicarboxylic acid (H_2TDA , **55b**) [126]. The synthesis used $\text{Zn(NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as the metal source and was carried out in DMF. Compound **55** could be employed as a multifunctional luminescent probe sensitive to Ag^+ cations (Table 6, Entry 21), $\text{Cr}_2\text{O}_7^{2-}$ anions (Table 6, Entry 21), and trinitrophenol (TNP) (Table 7, Entry 27). The detection mechanism was based on luminescence quenching of compound **55** suspensions in DMF in the presence of the analytes. An exception was the cation-detection studies, which were carried out in aqueous suspensions of compound **55** activated by guest-exchange treatment, replacing DMF with dichloromethane (DCM).

Table 4. Luminescence properties of cluster-based MOFs containing 1,2,4-triazole.

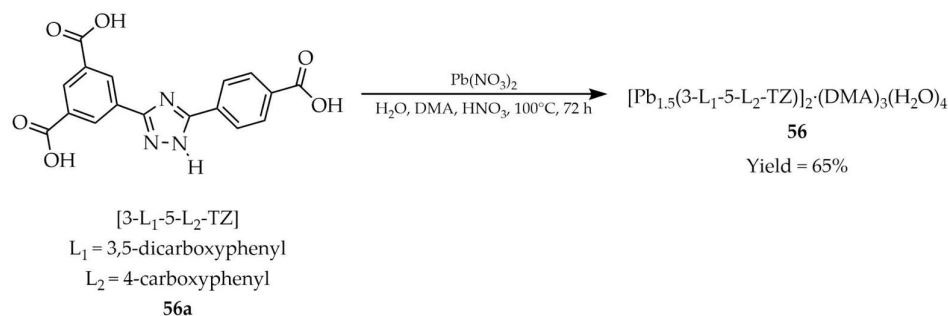
Cluster-Based Metal–Organic Frameworks				
MOF	λ_{abs} [nm]	λ_{ex} [nm]	λ_{em} [nm]	Ref.
50	-	284 ^a , 334 ^b	339 ^a , 382 ^b	[121]
50a	-	284 ^a , 334 ^b	355 ^a , 390 ^b	
51	-	320 ^c , 320 $\pm$ 5 ^e	422 ^c , 450 ^e	[122]
51a	-	320 ^d , 320 $\pm$ 5 ^e	388 ^d , 402 ^e	
52 ^e	-	284	347	[123]
53 ^e	-	357	595, 620, 650, 700	[124]
53a ^e	-	370	504	
55 ^e	-	366	428	[126]
55a ^e	-	442	493	
55b ^e	-	349	402	

^a suspension in acetonitrile; ^b suspension in water; ^c suspension in DMF; ^d solution in DMF; ^e solid state.

**Scheme 43.** Formation of a zinc-based framework (**55**) using 1*H*-3,5-bis(4-pyridyl)-1,2,4-triazole (**55a**) and thiophene-2,5-dicarboxylic acid (**55b**).

3.1.5. Lead-Based Metal–Organic Frameworks Containing 1,2,4-Triazole Linker

In 2019, Sun and coworkers described metal–organic frameworks based on lead(II), $[\text{Pb}_{1.5}(3\text{-}L_1\text{-}5\text{-}L_2\text{-TZ})_2]_2 \cdot (\text{DMA})_3(\text{H}_2\text{O})_4$ (**56**, Scheme 44), synthesized using the polycarboxylate ligand 3-(3,5-dicarboxylphenyl)-5-(4-carboxylphenyl)-1*H*-1,2,4-triazole ($[3\text{-}L_1\text{-}5\text{-}L_2\text{-TZ}]$, $L_1 = 3,5\text{-dicarboxylphenyl}$, $L_2 = 4\text{-carboxylphenyl}$], **56a**). The reaction was carried out with $\text{Pb}(\text{NO}_3)_2$, *N,N*-dimethylacetamide (DMA) and water with the addition of HNO_3 as the reaction medium [127]. The developed material **56** exhibited two luminescence emission maxima at 380 nm ($\lambda_{\text{ex}} = 280$ nm) and 540 nm ($\lambda_{\text{ex}} = 380$ nm) (Table 5). Tests performed in a series of solvents (H_2O , EtOH, MeOH, DMF, DMA) revealed luminescence quenching by dimethylaniline (DMA), observed for the emission peak at 380 nm ($\lambda_{\text{ex}} = 280$ nm), while the opposite effect, i.e., luminescence enhancement, was observed at 540 nm ($\lambda_{\text{ex}} = 380$ nm). Metal cation detection experiments were also carried out, and among the twenty-three tested cations four ions: Fe^{3+} , In^{3+} , Zr^{4+} and Al^{3+} induced a pronounced decrease in luminescence intensity (Table 6, Entry 22) in aqueous suspensions at an excitation wavelength of 280 nm. Compound **56** was also investigated for detection of selected drugs, aromatic, and nitroaromatic compounds (Table 7, Entry 28). As a result, five substances were identified with the best detection performance: metronidazole (MNZ), dimetridazole (DTZ), 2,4,6-trinitrophenol (TNP), 4-nitroaniline (4-NA), and nitrobenzene (NB).



Scheme 44. Synthesis of a lead-based MOF (**56**) from 3-(3,5-dicarboxyphenyl)-5-(4-carboxyphenyl)-1H-1,2,4-triazole (**56a**).

3.1.6. Cobalt-Based Metal–Organic Frameworks Containing 1,2,4-Triazole Linker

In 2021, Chand and coworkers described an anionic MOF $\{[\text{Me}_2\text{NH}_2]_{0.5}[\text{Co}(\text{3,5-NH}_2\text{-TZ})_{0.5}(\text{NH}_2\text{BDC})] \cdot x\text{G}\}_n$ (G = guest molecule) (**57**, Scheme 45), synthesized from 3,5-diamino-1,2,4-triazole ($[\text{3,5-NH}_2\text{-TZ}]$, **57a**) and 2-amino-1,4-benzenedicarboxylic acid ($\text{H}_2\text{NH}_2\text{-BDC}$, **57b**) [128]. The reaction was carried out with hydrated cobalt salt $\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$ in DMF. The selected components contain free amino groups, which, together with Me_2NH_2^+ cations, enable the binding of guest molecules within the pores. Material **57** exhibited blue luminescence (Table 5) and showed increased luminescence intensity in the presence of Al^{3+} cations (Table 6, Entry 23). This allowed detection at very low concentrations down to 17.5 ppb, without interference from other metal cations present in the sample, indicating sensitive and selective detection. A practical aspect of the study was also demonstrated by applying compound **57** onto filter paper, enabling its use as a simple test for Al^{3+} cations, with a bright luminescent signal under UV light (365 nm) visible to the naked eye in real time. An enhancement of luminescence was also observed in the presence of the Lewis acid boron trifluoride (BF_3).



Scheme 45. Synthesis of a cobalt-based framework (**57**) using 3,5-diamino-1,2,4-triazole (**57a**) and 2-amino-1,4-benzenedicarboxylic acid (**57b**).

3.1.7. Copper-Based Metal–Organic Frameworks Containing 1,2,4-Triazole Linker

In 2019, Qian and coworkers described the synthesis of MOF based on copper(II) $\{[\text{Cu}((1\text{-L}_1\text{-TZ})_3\text{N})(\text{pim})] \cdot \text{H}_2\text{O}\}_n$ (**58**, Scheme 46) using tris(4-(1,2,4-triazol-1-yl)phenyl)amine ($[(1\text{-L}_1\text{-TZ})_3\text{N}]$, $\text{L}_1 = 4\text{-phenyl}$], **58a**) and pimelate (pim , 1,5-pentanedicarboxylate, **58b**) [129]. The reaction was performed with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in the presence of NaOH using a solvent mixture of water, methanol, and DMF. The obtained material **58** exhibited luminescent properties (Table 5) but the studies particularly focused on its photocatalytic ability to degrade selected organic dyes. The degradation efficiency of methylene blue under visible light irradiation reached 90.3% after 75 min, while for rhodamine B (RhB), 90.1% degradation was achieved after 150 min. Compared to commercially available TiO_2 , better results were obtained. The photocatalytic mechanism was thoroughly discussed and confirmed by experiments using different scavengers such as mannitol, terephthalic acid, ammonium oxalate, and benzoquinone. These results highlight the potential application of this MOF for the removal of dye pollutants from water under visible light.

Table 5. Luminescence properties of other metal-based MOFs containing 1,2,4-triazole.

Other M-Based Metal–Organic Frameworks					
M	MOF	λ_{abs} [nm]	λ_{ex} [nm]	λ_{em} [nm]	Ref.
Pb	56 ^a	-	280	380	[127]
	56 ^a	-	380	540	
	56a ^a	-	280	~400	
Co	57 ^a	-	340	430	[128]
Cu	58 ^a	512	330	412	[129]
	58a ^a	-	310	411	

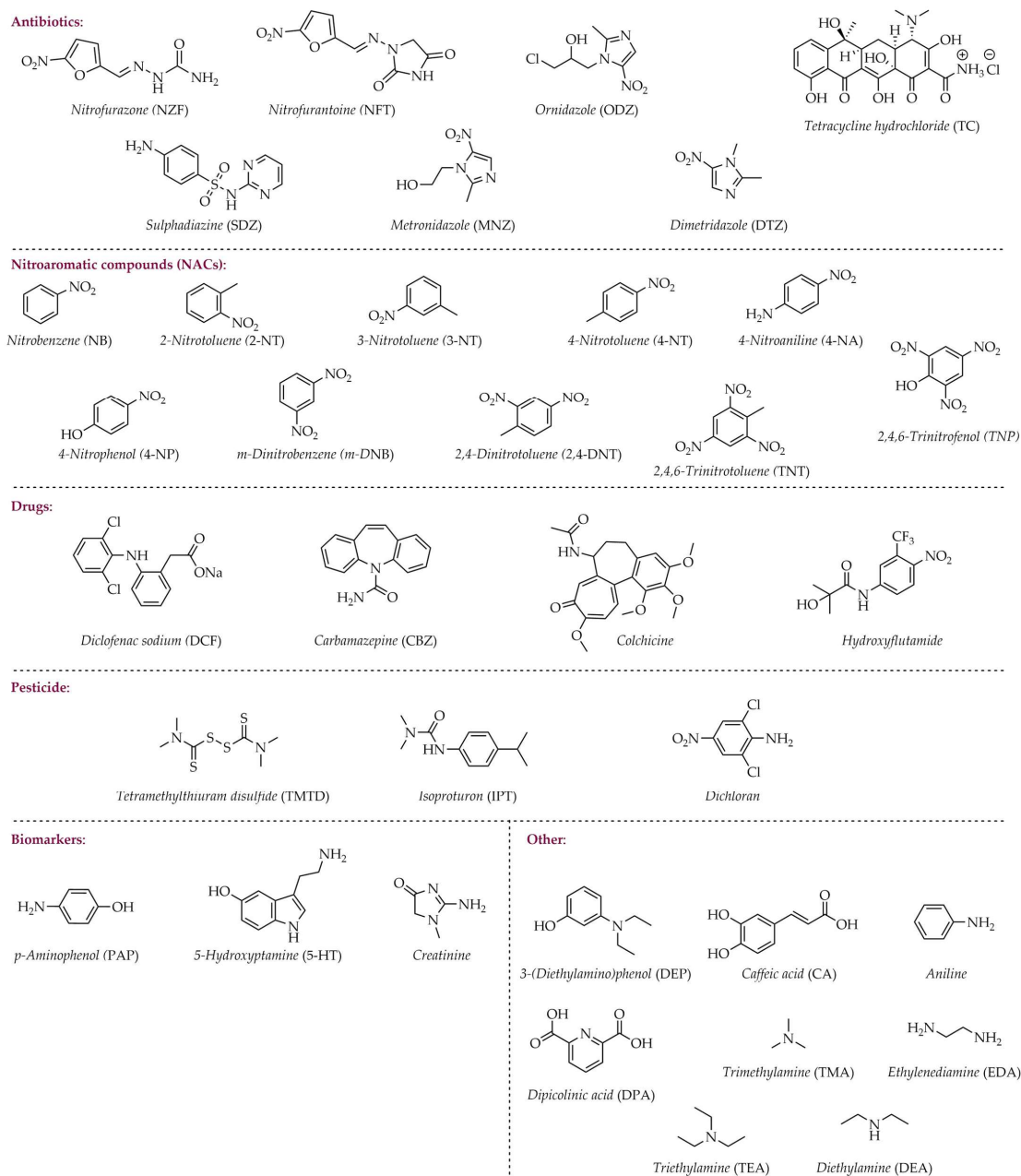
^a solid state.**Figure 8.** Examples of various organic compounds that can be detected using luminescent 1,2,4-triazole-based MOF sensors.

Table 6. 1,2,4-Triazole-based MOFs as luminescent sensors for metal cations and anions.

Entry	MOF	Sensing of Cations			Sensing of Anions			Ref.
		Cation	K_{sv} [L/mol]	Detection Limit [mol/L] or ppm	Anion	K_{sv} [L/mol]	Detection Limit [mol/L] or ppm	
1	5 ^a	Fe ³⁺	1.01×10^4	4.61×10^{-6}	Cr ₂ O ₇ ^{2−}	1.24×10^4	2.55×10^{-6}	[90]
		Al ³⁺	-	4.43×10^{-6}	SiF ₆ ^{2−}	-	1.35×10^{-5}	
2	6 ^a	-	-	-	Cr ₂ O ₇ ^{2−}	9.72×10^3	5.82×10^{-4}	[91]
3	7 ^b	Ni ²⁺	9.81×10^4	0.46×10^{-6}	PO ₄ ^{3−}	6.91×10^3	6.5×10^{-6}	[92]
4	8 ^c	Cu ²⁺	5.96×10^4	0.76×10^{-6}	MnO ₄ [−]	2.00×10^5	6.14×10^{-6}	[93]
		Ag ⁺	1.67×10^4	6.40×10^{-6}	Cr ₂ O ₇ ^{2−}	1.85×10^5	13.64×10^{-6}	
		-	-	-	CrO ₄ ^{2−}	5.89×10^4	12.33×10^{-6}	
5	13 ^d	Fe ³⁺	4.85×10^4	-	-	-	-	[97]
6	14 ^e	Fe ³⁺	4.22×10^3	0.92×10^{-9}	-	-	-	[98]
7	16 ^f	Fe ³⁺	7.69×10^4	0.58×10^{-6}	Cr ₂ O ₇ ^{2−}	3.28×10^4	1.37×10^{-6}	[100]
8	16d ^f	Fe ³⁺	4.61×10^4	0.98×10^{-6}	Cr ₂ O ₇ ^{2−}	2.16×10^4	2.08×10^{-6}	
9	17 ^a	Fe ³⁺	2.21×10^4	1.85×10^{-6}	Cr ₂ O ₇ ^{2−}	1.02×10^4	2.21×10^{-6}	[101]
		-	-	-	CrO ₄ ^{2−}	1.26×10^4	3.78×10^{-6}	
10	21 ^a	Cu ²⁺	3.83×10^4	1.39×10^{-6}	-	-	-	[105]
11	25c ^a	Fe ³⁺	1.13×10^4	0.098	Cr ₂ O ₇ ^{2−}	5.42×10^4	0.32	[107]
		-	-	-	CrO ₄ ^{2−}	1.73×10^4	0.28	
12	27 ^e	Cr ³⁺	4.39×10^3	10.25×10^{-6}	Cr ₂ O ₇ ^{2−}	1.49×10^5	9.18×10^{-6}	[108]
		-	-	-	CrO ₄ ^{2−}	4.90×10^3	0.3×10^{-6}	
13	29 ^a	Ag ⁺	8.16×10^3	1.4×10^{-6}	-	-	-	[99]
14	36 ^a	-	-	-	PO ₄ ^{3−}	1.27×10^4	2.74×10^{-4}	[112]
15	41 ^e	-	-	-	MnO ₄ [−]	1.69×10^4	1.6×10^{-4}	[114]
16	2 ^{f,g}	Fe ³⁺	1.03×10^4	8.78×10^{-3}	-	-	-	[51]
17	3 ^{f,h}	Fe ³⁺	1.49×10^4	8.60×10^{-3}	-	-	-	
18	45 ^a	Fe ³⁺	7.36×10^3	0.57×10^{-6}	Cr ₂ O ₇ ^{2−}	4.85×10^3	2.29×10^{-6}	[118]
19	46 ^a	Fe ³⁺	1.18×10^4	0.93×10^{-6}	Cr ₂ O ₇ ^{2−}	1.37×10^4	1.54×10^{-6}	
20	54 ^a	-	-	-	Cr ₂ O ₇ ^{2−}	1.22×10^4	0.023×10^{-6}	[125]
21	55	Ag ⁺ ^a	1.751×10^5	5.96×10^{-6}	Cr ₂ O ₇ ^{2−} ^f	7.397×10^4	4.34×10^{-6}	[126]
22	56 ^a	Fe ³⁺	1.2×10^5 ⁱ	2.5 ⁱ	-	-	-	[127]
			4.2×10^3 ^j	71 ^j	-	-	-	
	56 ^a	In ³⁺	1.6×10^5 ⁱ	-	-	-	-	
	56 ^a	Zr ⁴⁺	1.6×10^5 ⁱ	-	-	-	-	
	56 ^a	Al ³⁺	4.3×10^4 ⁱ	-	-	-	-	
23	57 ^f	Al ³⁺	-	0.0175	-	-	-	[128]

^a suspension in aqueous solution; ^b soaked in different M(NO₃)_x solution; ^c ground sample immersed in 1 mL DMF: H₂O (*v/v* = 1:1); ^d immersed in DMF; ^e immersed in aqueous solution; ^f suspension in DMF; ^g based on the luminescence intensity at 613 nm; ^h based on the luminescence intensity at 545 nm; ⁱ λ_{ex} = 280 nm; ^j λ_{ex} = 380 nm.

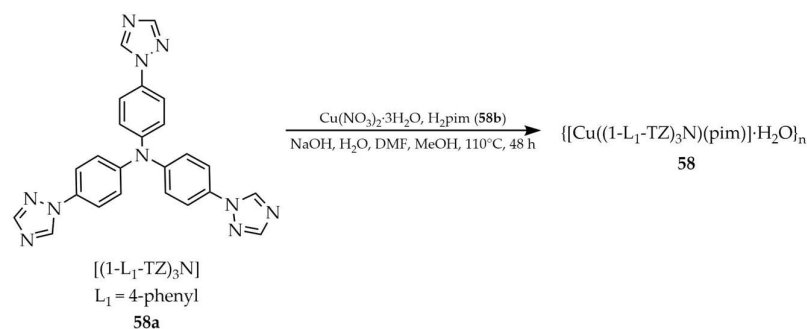
Table 7. 1,2,4-Triazole-based MOFs as luminescent sensors for different organic compounds (drugs, antibiotics, pesticides, NACs, etc.).

Entry	MOF	Detected Compound	K_{SV} or K_{EC} [L/mol]	Detection Limit [mol/L] or ppm	Ref.
1	5 ^a	NZF	5.2×10^4	4.04×10^{-7}	[90]
		NFT	1.8×10^5	3.53×10^{-7}	
2	13 ^b	NB	8.58×10^3	-	[97]
3	17 ^a	PAP	1.95×10^4	3.53×10^{-6}	[101]
		NZF	5.50×10^4	0.46×10^{-6}	
4	18b ^c	DCF	4.32×10^4	0.62×10^{-6}	[102]
		TMTD	3.10×10^4	0.76×10^{-6}	
5	21b ^a	arginine	2.76×10^4	0.69	[104]
6	18 ^a	TNP	1.63×10^4	3.11×10^{-7}	[105]
7	18 ^d	TNP	2.99×10^4	5.95×10^{-7}	
		4-NP	3.84×10^3	2.53×10^{-6}	
		2,4-DNT	3.76×10^3	3.47×10^{-6}	
		NB	5.49×10^3	2.61×10^{-6}	
		4-NT	4.54×10^3	3.31×10^{-6}	
		1,3-DNB	5.21×10^3	2.58×10^{-6}	
8	24 ^a	acetone	12.89	-	[106]
9	28b ^d	DEP	3.74×10^5	79.8×10^{-9}	[109]
		IPT	1.82×10^3	2.26×10^{-7}	
		dichloran	3.88×10^4	1.24×10^{-7}	
10	29 ^d	4-NP	4.37×10^4	3.29×10^{-7}	[99]
11	35 ^a	TC ^e	4.06×10^4	0.887	[111]
		NZF ^e	1.03×10^4	2.770	
		NFT ^e	1.90×10^5	0.189	
		SDZ ^e	1.90×10^4	1.890	
		CBZ ^e	9.64×10^4	0.373	
		MNZ ^f	1.66×10^5	0.217	
		DTZ ^f	1.64×10^5	0.219	
		ODZ ^f	2.54×10^5	0.142	
12	36 ^a	acetylacetone	3.22×10^2	1.21×10^{-4}	[112]
13	41 ^d	m-DNB	3.08×10^2	0.23×10^{-3}	[114]
		NB	2.26×10^3	0.19×10^{-3}	
		4-NT	4.01×10^3	0.10×10^{-3}	
		2,4-DNT	4.45×10^3	0.22×10^{-3}	
		TNP	9.10×10^3	0.17×10^{-3}	
		4-NP	3.38×10^4	0.20×10^{-3}	
14	42 ^a	creatinine	5.1×10^{-3}	1.7×10^{-6}	[115]
15	43 ^a	colchicine	57,963	2.43×10^{-5}	[116]

Table 7. Cont.

Entry	MOF	Detected Compound	K _{SV} or K _{EC} [L/mol]	Detection Limit [mol/L] or ppm	Ref.
16	2 ^{d,g}	2-NT	9.01×10^3	4.58×10^{-5}	[51]
		3-NT	28.43×10^3	1.53×10^{-5}	
		4-NT	27.87×10^3	2.01×10^{-5}	
		4-NP	10.76×10^3	7.68×10^{-6}	
17	3 ^{d,e}	2-NT	8.01×10^3	1.44×10^{-5}	
		3-NT	40.87×10^3	5.60×10^{-6}	
		4-NT	30.59×10^3	8.30×10^{-6}	
		4-NP	11.81×10^3	2.85×10^{-6}	
18	44 ^h	hydroxyflutamide	4.98×10^{12}	8.37×10^{-15}	[117]
19	44b ⁱ	PSA	7.9×10^{10}	4.99×10^{-13}	
		AR	2.9×10^8	0.14×10^{-9}	[118]
20	45 ^a	TNP	6.93×10^3	1.63×10^{-6}	
21	46 ^a	TNP	1.21×10^4	1.35×10^{-6}	[119]
22	49 ^d	CA	2.49×10^5	36.4×10^{-9}	
23	50	TNP	7.66×10^4 ^j 6.36×10^4 ^a	0.81×10^{-6} ^j 0.66×10^{-6} ^a	[121]
		NB	3.94×10^4 ^j	1.00×10^{-6} ^j	
		2,4-DNT	3.10×10^4 ^j	1.11×10^{-6} ^j	
		TNT	1.18×10^4 ^j	2.15×10^{-6} ^j	
24	52 ^a	5-HT	6.00×10^4	0.040×10^{-3}	[123]
		DPA	6.30×10^4	0.078×10^{-3}	
25	53 ^k	EDA	8.08×10^3	4.29×10^{-7}	[124]
		DEA	6.15×10^3	4.94×10^{-7}	
		TMA	4.83×10^3	5.89×10^{-7}	
		TEA	2.92×10^3	9.84×10^{-7}	
		aniline	2.46×10^3	1.012×10^{-6}	
26	54 ^a	DPA	1.48×10^5	0.298×10^{-6}	[125]
27	55 ^d	TNP	1.856×10^5	1.59×10^{-6}	[126]
28	56 ^a	TNP	3.3×10^4 ^k	9	[127]
			3.6×10^4 ^l	8	
		4-NA	2.3×10^4 ^k	13	
			2.4×10^4 ^l	12.5	
		NB	1.5×10^4 ^k	20	
			0.7×10^4 ^l	43	
		MNZ	1.3×10^4 ^k	23	
			1.5×10^4 ^l	20	
		DTZ	0.9×10^4 ^k	33	
			1.5×10^4 ^l	20	

^a suspension in aqueous solution; ^b immersed in DMF; ^c suspension in MeOH/isopropanol ($v/v = 4:1$); ^d suspension in DMF; ^e based on the luminescence intensity at 545 nm; ^f based on Tb³⁺ component; ^g based on the luminescence intensity at 613 nm; ^h DMSO solution; ⁱ human serum aqueous solution 10%; ^j suspension in acetonitrile; ^k ethanol emulsion; ^k $\lambda_{\text{ex}} = 280$ nm; ^l $\lambda_{\text{ex}} = 380$ nm.



Scheme 46. Preparation of a copper-based MOF (58) from tris(4-(1,2,4-triazol-1-yl)phenyl)amine (58a) and pimelate (58b).

4. General Remarks on Structure-Property Relationships and Current Challenges for 1,2,4-Triazole-Based LMOFs

The diversity of methodologies available for constructing the 1,2,4-triazole heterocyclic ring enables the synthesis of numerous derivatives exhibiting valuable properties for a wide range of applications. Among these are luminescent metal–organic frameworks (LMOFs), which can serve as functional materials for OLED fabrication and luminescent sensing, offering an attractive alternative to existing material solutions. Table 8 presents the influence of the metal center, ligand structure, and reaction medium on luminescence efficiency. In general, the 1,2,4-triazole core is characterized by high physical and chemical stability, as well as the ability to form coordination bonds with metals due to the presence of nitrogen atoms in the ring. The coordination potential can be further enhanced by incorporating additional heterocycles, such as pyridine or imidazole, or functional groups such as amino and carboxyl groups into the ligand structure. The most important feature of these ligands determining the luminescent properties of the resulting material is the presence of an extended conjugated system, provided mainly by aromatic rings, which enables excitation and subsequent emission of radiation. For this reason, alkyl substituents are generally not employed in the design of such structures, and the triazole ring alone is rarely used. In the case of lanthanide-based MOFs, an antenna effect is observed, in which the organic ligand sensitizes the metal center, and the resulting emission spectrum contains only the characteristic bands of the metal ion. Consequently, as shown in Table 8, these materials exhibit exceptionally high quantum yields (9.5–52.51%) and long luminescence lifetimes (143,000–1,150,000 ns). A crucial factor in the successful commercialization of these technologies is the ability to scale the process from laboratory to industrial level. The synthesis of 1,2,4-triazole-based ligands typically involves a multistep sequence of transformations, which reduces the overall yield, increases costs, and may impose an environmental burden. The study indicates that the solvothermal method is the most frequently employed approach for synthesizing MOFs based on this organic ligand, using solvents such as DMF, water, methanol, DMSO, DMA, ethanol, acetonitrile, and DMAC. The advantages of this method include moderate-to-excellent product yields (15–99%), control over structural features such as morphology and porosity, and the use of inexpensive, readily available, and environmentally benign inorganic salts. However, this is a high-pressure process, which poses a challenge for large-scale manufacturing. Furthermore, it necessitates the use of organic solvents of varying toxicity; therefore, more sustainable routes compliant with current environmental regulations include hydrothermal synthesis or the use of regenerable ionic liquids. An equally promising alternative involves electrochemical methods, which enable reactions to proceed under ambient pressure and at room temperature. The current research efforts on triazole-based LMOFs should be directed toward developing more efficient and environmentally friendly synthetic strategies for

ligand preparation and evaluating the effectiveness of the proposed methodologies for producing such porous materials.

Table 8. The influence of the metal center and ligand structure on luminescence efficiency.

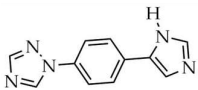
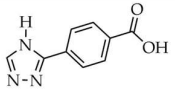
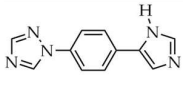
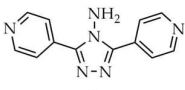
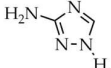
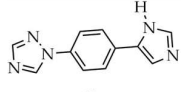
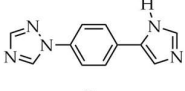
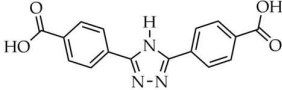
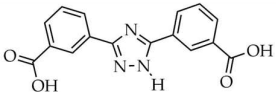
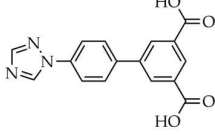
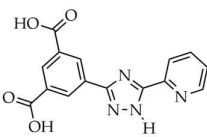
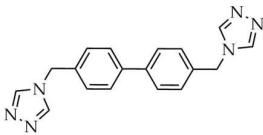
Metal	Ligand	Medium	MOF	Quantum Yield [%]	Luminescence Lifetime [ns]	Ref.
Zn	 10a	H ₂ O	10	5.24	29.56	[95]
			11	3.18	18.53	
	 13a	DMA/ toluene	13	7.4	-	[97]
	 15a	DMF/ EtOH/ H ₂ O	15	2.15	8	[99]
	 16a	DMF/ EtOH	16	18	6.27	[100]
			16c	25.3	484,500, 1,260,700	
	 19a	DMF/ H ₂ O	19c	3.02	2.7241	[103]
Cd	 10a	H ₂ O	26	2.62	14.62	[95]
	 15a	H ₂ O	29	5.32	16	[99]
Tb	 41a	DMF/ H ₂ O	41	9.5	143,000	[114]
Eu	 43a	H ₂ O	43	52.51	726,000	[116]
Eu, Tb	 44a	DMF/ H ₂ O	44	42	544,000	[117]

Table 8. Cont.

Metal	Ligand	Medium	MOF	Quantum Yield [%]	Luminescence Lifetime [ns]	Ref.
Eu	 45a	CH ₃ CN/H ₂ O	45	9.8	1,150,000	[118]
Tb			46	10.1	940,000	
Cu	 51a	MeOH/ H ₂ O	51	4.81	1.46	[122]

5. Conclusions

Metal–organic frameworks (MOFs) represent a broad class of materials with diverse application potential, ranging from energy storage systems and catalysis to gas separation. The specific field of application depends on their physicochemical properties, which can be tuned by the appropriate selection of metal nodes forming the structure and the organic ligands connecting them. A special class of organic compounds used as ligands in the construction of such materials consists of five-membered 1,2,4-triazoles conjugated with other aromatic or heteroaromatic rings and substituted with amino or carboxylic groups. Studies conducted between 2019 and 2025 have highlighted their usefulness in the construction of LMOFs incorporating *d*-block transition metals such as zinc, cadmium, cobalt, and copper; *f*-block lanthanides including europium, gadolinium, terbium, lanthanum, holmium, and dysprosium; as well as lead and metal clusters. In addition to their luminescent properties, many of the reported MOFs exhibit sensitive and selective detection capabilities toward metal cations and anions, pharmaceuticals, pesticides, and nitroaromatic compounds (NACs), which are important environmental pollutants. Promising results have also demonstrated the effectiveness of 1,2,4-triazole-based MOFs as luminescent probes for various biomolecules, indicating their high potential in medical diagnostics. Moreover, some of these materials display high color purity of emitted light, making them attractive candidates for integration into OLED devices. Future perspectives for 1,2,4-triazole-based LMOFs include their incorporation with optical sensors and electronic components to construct integrated devices for the detection of harmful substances in food and drinking water. The development of such technologies could enable the creation of a new generation of biosensors synchronized with smartphone applications, providing an innovative approach to health monitoring.

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