Chapter

Supramolecular Assembly of Benzimidazole Derivatives and Applications

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Abstract

Herein, we focus on the chemical and physical properties of benzimidazole and its derivatives used for the synthesis of supramolecular materials. The design and modification of benzimidazole opens the scope of the diversity of structures (different sizes and morphologies) that can be built. The synthesized materials include not only small coordination complexes but also isolated crystals, metal-organic frameworks, metal-coordination polymers, smart nanocontainers, and more advanced macrostructures such as microflowers and nanowires. These supramolecular structures are based on noncovalent interactions, mostly on metal coordination chemistry and $\pi-\pi$ stacking interactions. Moreover, the same molecule, due to its chemical structure, can undergo both sorts of interactions in order to induce the self-assembly into supramolecular materials. In this process, as it is shown in this chapter, the conditions used for the assembly determine the final structure and morphology of the fabricated macromolecule. Finally, we show most recent applications of these materials in the field of sensing, photoluminescence, fuel cell, and fabrication of new nanostructures.

Keywords: self-assembly, supramolecular interactions, metal-imidazole coordination, $\pi-\pi$ stacking interactions

1. Introduction

Benzimidazole and its derivatives are mostly known by their role in therapeutic drugs and by their pharmacological activities, for example, antimicrobial, analgesic, and anti-inflammatory [1]. Moreover, they are part of essential biomolecules as vitamin $B_{12}$ [2]. Thus, the biological activity of benzimidazole and its derivatives is unquestionable. However, there is a growing research interest in using benzimidazole derivatives for their assembly into supramolecular structures for technological applications. This implies the formation of well-defined complex bond through noncovalent interactions. In this regard, the interest on benzimidazole molecule is twofold (Figure 1). On the one hand, benzimidazole is a popular N-donor ligand that is often used in coordination chemistry, meaning that it can through metal- or small-molecule coordination to the assembly of molecules. Indeed, the imidazole ring is commonly found as part of essential components of biological products,
**Figure 1.**
The physicochemical nature of benzimidazole allows the assembly through different chemistries such as hydrophobic interactions (mainly through the benzyl group) and small-molecule coordination (mainly through the imidazole ring). Benzimidazole derivatives (different “R”) will lead to the synthesis of assemblies of diverse composition and thus morphology and properties.

| Type of material         | Assembly                              | Ligand                                                                 | Application                                      | Reference |
|--------------------------|---------------------------------------|------------------------------------------------------------------------|--------------------------------------------------|-----------|
| Metalogel                | Metal-metal, hydrophobic interactions | 2,6-Bis(benzimidazol-2’-yl)pyridine                                   | Nanocontainer for small molecules                | [4–6]     |
| Macrocycles              | Anion binding coordination            | N-methylbenzimidazole                                                 | Tautomer switch                                 | [7]       |
| Coordination polymer     | Metal coordination, Ag(I), Cu(II), lanthanides (III), hydrophobic interaction | N,N′-bisoctadecyl-2-(1H-benzimidazol-2-carbonyl)-L-glutamic amide        | Chiral materials, photoluminiscence              | [8]       |
| Metal-organic crystals   | Metal coordination, Cu(II), Zn(II)    | 1-Benzylamonium                                                       | Photoluminiscence                                | [9]       |
| Metal-organic frameworks | Metal coordination, Cd(II)             | 2-Pyridin-3-yl-1H-benzoimidazole                                      | Photoluminiscence                                | [10]      |
| Metal-organic frameworks | Metal coordination, Cd(II)             | 2-Pyridin-4-yl-1H-benzoimidazole                                      | Photoluminiscence                                | [11]      |
| Metal-organic frameworks | Metal coordination, Ag(I)              | 2-Heptadecylbenzimidazole                                             | Dye adsorption                                   | [12]      |
| Coordination polymer     | Metal coordination, Cd(II)             | 1H-benzimidazole-5-carboxylic acid                                    | Fluorescence                                     | [13]      |
| Metal-organic frameworks | Metal coordination, Cd(II)             | 1,1′-((1,5-Pentanediyl) bis-1H-benzimidazole)                         | Photoluminiscence                                | [14]      |
| Coordination polymer     | Metal coordination, lanthanides (III) | Tris(benzimidazole-2-ylimethyl) amine                                 | Adsorbent materials                              | [15]      |
| Coordination polymer     | Metal coordination, Zn(II) and Cd(II)  | 3-(1H-benzoimidazol-2-yl) propanonic acid                             | —                                                | [16]      |
| Coordination polymer     | Metal coordination, Co(II)             | 1,1-(1,4-Butanediyl) bis-1H-benzimidazole                             | —                                                | [17]      |
| Coordination polymer     | Metal coordination, Cd(II)             | 1,3-Bis(5,6-dimethylbenzimidazole) propane                            | Photoluminiscence                                |           |
|                          |                                       | 1,4-Bis(5,6-dimethylbenzimidazole) butane                             |                                                   |           |
|                          |                                       | 1,6-bis(5,6-dimethylbenzimidazole) hexane                             |                                                   |           |
such as histidine (in proteins), purine, histamine, and nucleic acids. In the specific case of proteins, it is common to find the imidazole ring in coordination with metal cations, which are essential for their biological function. On the other hand, the benzyl ring of the benzimidazole can undergo physical interactions (hydrophobic, π-π interactions) with other planar benzyl groups or hydrophobic moieties. Moreover, the controlled intra- and intermolecular π-π interactions can lead the supramolecular assembly into large structures.

Supramolecular assemblies are emergent structures basically driven by physical interactions [3]. It consists in a controlled multilevel organization process, from the assembly of discrete elementary molecular units via noncovalent interaction, to the further assembly of those into complex functional structures. The interaction forces operate under entropic constraints, looking for energy minimization. Selected organic and/or inorganic molecules can determine the chemical and structural composition of the eventually formed material. Therefore, this is a versatile methodology for the fabrication of nano-microstructures of defined size, morphology, and properties.

In this chapter, we show different approaches that are currently utilized for the controlled assembly of benzimidazole and its derivatives for the formation of large and ordered structures. Derivatives of imidazole are specifically designed for the assembly into structures with diverse size and morphology [4]. We will go through the methodologies that allow the fabrication of isolated crystals, metal-coordinated polymers, metal-organic frameworks, helical structures, smart nanocontainers, and advanced structures such as microflowers or nanowires. Moreover, benzimidazole can be combined with biological macromolecules (proteins, nucleic acid) to trigger their assembly. Finally, we show that benzimidazole derivatives, besides the key role they have shown in the self-assembly of macromolecules, are used in a reasonably broad range of technological applications such as sensing, photoluminescence, fuel cell, and fabrication of new nanostructures. A list of examples in which benzimidazole molecule is used for the assembly into supramolecular structures are summarized in Table 1.

| Type of material | Assembly | Ligand | Application | Reference |
|------------------|----------|--------|-------------|-----------|
| Macrocycles and large structures | Metal coordination, Co(II) | 1,1′-(1,4-butanediyl) bis(benzimidazole) | Thermostable polymers | [18] |
| Helical coordination polymers | Metal coordination, Cd(II), Zn(II) | 1,1-(1,4-Butanediyl) bis-1H-benzimidazole | Electrochemistry | [19] |
| Self-assembled polymer | Hydrophobic interactions | 4-(1H-Benzimidazole-2-yl)-benzoic acid | Integration in functional devices | [20] |
| Metal-organic macrocycles | Metal coordination-Pd(II)-anion binding | di-Benzimidazole | Nanocontainers | [21] |
| Conjugates of calix-6-arenes | Covalent | (Tris)imidazole | Cu sensor | [22] |
| Liquid polymers | Hydrogen bonding | 40-(6-(Benzimidazolethio) hexoxy)-diphenyl-4-yl 4-(alkoxy) benzate | Liquid crystals for electronic conduction | [23] |
| Coordination polymer | Metal coordination, Zn(II) | 2,6-bis(1′-methylbenzimidazolyl) pyridine | Self-healing material | [24] |

Table 1. Examples of materials synthesized through supramolecular assembly of benzimidazole derivatives.
2. Supramolecular self-assembly through coordination chemistry

The combination of organic and inorganic compounds to raise supramolecular structures is an on-growing research field. This approach broadens the applications and the nature of the morphologies and chemistries that can be applied for. Of particular importance is the assembly of metal (inorganic)-organic structures based on coordination chemistry. A good design of the ligands and metal cations and the selection of the appropriate synthesis method can lead to the formation of well-defined crystals, frameworks, or polymers as it is discussed below. Furthermore, the anion binding chemistry is another field of application of coordination chemistry. Small molecules such as anions coordinate to ligands to form stable complexes with interesting properties.

In this section, we focus on the ability of the imidazole ring to coordinate to small molecules such as anions and metal ions for the formation of discrete complexes and large supramolecular structures.

2.1 Supramolecular assembly with small molecules

The field of the coordination chemistry compiles a broad range of interactions, from classical Werner transition metal complexes, clusters, and organometallics, to host-guest complexes and supramolecular complexes (e.g., crown ethers or cryptands) \[25\]. Usually, in most of the examples found in the literature, benzimidazole derivatives are coordinated through metal-cation interaction. However, the anion binding chemistry has an important impact within the coordination chemistry field and, as it is going to be shown below, in the formation of discrete complexes and large supramolecular assemblies with benzimidazole derivatives.

Anionic species are generally larger than metal cations and thus might require greater size of the ligands. Moreover, the coordination of anions is usually saturated and therefore they only interact with ligands via weak forces, that is, hydrogen bonding and van der Waals interactions. Additionally, the relatively narrow pH window in which many anions exist determines the stability of the synthesized complexes. Anions play significant roles in biology, as receptors or cofactors, and in a broad number of applications such as sensing, crystal engineering, transmembrane transport, or anion-based catalysis \[26\].

Imidazole and benzimidazole derivatives have been used as ligands in anion binding-coordinated complex formation. In the case of imidazole molecule, both the nitrogen atoms within the imidazole ring are both covalently bond to sp3-hybridized carbon atoms. In these systems, the positively charged imidazolium group works as a hydrogen bond donor, interacting with the coordinated anion through a combination of hydrogen bonding and electrostatic interactions \[7\].

Furthermore, when using benzimidazole units, those can be employed as NH hydrogen bond donors and, in this case, a tautomerism process may affect the nature of the hydrogen bond presented to an anionic guest. As example, the N-methylbenzimidazole-based ligands selectively interact with the dihydrogen phosphate ion, acting as both a hydrogen bond donor and acceptor. Hence, several receptors containing benzimidazole derivatives have been reported as colorimetric, fluorescent, and electrochemically active sensors (Table 1).

2.2 Supramolecular assembly with metal cations

As a component of vitamin 1benzimidazole moiety exhibits good coordination ability with various transitional metal ions, such as Mn(II), Fe(II), Co(II), Ni(II), Cd(II), Hg(II), Pd(II), Cu(II), Zn(II), Ag(I), and Pb(II). In addition, it has
been shown to coordinate with rare earth metal ions (lanthanides) [8]. The metal coordination of the imidazole ring is used in nature for the hierarchical assembly of biopolymers, for example, mussel byssus or worm jaws, and metalloproteins, in which the metal cations can not only show a structural function, but also contribute in their functionality, for example, catalysis in enzymes.

The metal coordination chemistry is an advantageous and widely used approach for assembly. The metal-ligand bonds are usually stronger than anion binding coordination; they are highly directional and kinetically labile. This means that, from one side, the symmetry and stereochemical preference is usually imposed by the metal cation and that this process is governed by a thermodynamic control, which is usually dependent on pH variations. Finally, metal ions bring along their intrinsic reactivity (as Lewis acidity, redox reactivity), which can be transferred to the assembled material.

The aforementioned advantages of metal coordination have been exploited to arrange small organic ligands into well-defined assemblies, organized arrays, that is, metal-organic frameworks (MOFs) and polymers. These materials have found applications in the host-guest chemistry, sensing, storage/separation, and catalysis.

2.2.1 Metal-organic macrocycles

Benimidazole unit has been used for the formation of complexes using a very simple synthesis approach [27]. The assemblage into well-defined crystals is driven through the spontaneous metal coordination assembly at room temperature. As example, the combination of CuCl₂·6H₂O salt in a mixture of water/MeOH solution with benimidazole in a molar ratio of 1:4 [9, 28] derives into the formation of dark blue crystals that consisted in a complex with formula [Cu(bim)₄Cl₂]·2H₂O. Similar results are obtained by mixing ZnCl₂ in a DMF solution for the synthesis of crystals of [Zn(bim)₂Cl₂]·3H₂O.

Nevertheless, most of the cases require the derivatization of the benimidazole unit to allow its assembly into larger arrays, frameworks, and polymers as it is explained below.

2.2.2 Synthesis of metal-organic frameworks

The exploration of metal-organic frameworks (MOFs) has received much attention because of their well-defined architectures and wide range of potential applications in different fields. The assembly of transition metal cations such as Zn(II) and Cd(II) with multidentate nitrogen-containing ligands has produced various MOFs with fascinating metal coordination structures and luminescent and catalytic properties [10, 11, 29]. The selection of chelating or bridging organic linkers often favors a structure-specific assembly, guiding the eventual morphology of the formed macromolecule. The factors that govern the formation of such complexes are complicated and include not only the nature of the metal ions and the ligand structure but also anion-directed interactions, hydrogen bonds, van der Wall forces, and employed reaction conditions.

The design and prediction of MOFs with potential properties is still a challenge to date [12]. Usually, the synthesis of MOFs starts from stiff bridging ligands via relatively strong dative bonds. Nevertheless, it has been proven that the contribution of hydrogen-bonded interactions leads to highly stable and porous architectures. Thus, of extreme importance is the design of ligands that can eventually undergo stabilization interactions.

Benimidazole derivatives have been used for the synthesis Cd-based MOFs. Cd-containing structures, both discrete assemblies and infinite molecular
frameworks, have been released from and characterized due to their useful properties in catalysis, luminescent materials, NLO materials, phase transformation, and host-guest chemistry. The use of 1,1′-(1,5-pentanediyl)bis-1H-benzimidazole as ligand formed a supramolecular structure that showed photoluminescence properties, which could be modulated by the influence of different counterions [13]. This points out the influence of anions in the arrangement of the coordination molecules and thus the final structure of the macromolecules.

Changing from transition metals to lanthanides leads to new applications and properties. The benzimidazole derivative (tris(benzimidazole-2-ylmethyl)amine, ntb) has been utilized as ligand for the synthesis of lanthanide (Ln: Nd³⁺, Eu³⁺, Gd³⁺, and Er³⁺) coordination monomers ([Ln(ntb)(NO₃)₃]) that are further assembled via hydrogen bonding into three-dimensional (3D) frameworks [14]. Synthesis and crystallization conditions controlled the eventual morphology of the materials for each lanthanide used (monoclinic, hexagonal and cubic crystals). The Eu³⁺ and Nd³⁺ derivatives showed solid-state photoluminescence in the near-infrared and visible region. In this case, the use of benzimidazole derivatives for the synthesis of porous coordination frameworks is advantageous for the supraorganization of structures through hydrogen-bonded frameworks, which is known to provide highly stable porous structures.

2.2.3 Fabrication of metal coordination polymers

There is a strong controversy on the use of the terms metal-organic frameworks and metal coordination polymers to assign the arrangement of an array of ligands through noncovalent coordination using metal cations [30]. As the term, metal-organic framework is very much appropriate to use for three-dimensional networks, the formation of one-dimensional and two-dimensional extended structures such as layers is named metal coordination polymers.

As the structures of coordination polymers are strongly influenced by the organic ligands and metal ions [15, 16, 31], it is important to choose suitable ligands and metal ions under appropriate synthetic conditions in order to synthesize coordination complexes with interesting structures. The flexibility of the ligand is a key parameter to direct the assembly into polymers instead of frameworks [17].

In this field, the synthesis of flexible divergent ligands is preferred. As example, the introduction of butane moieties to benzimidazole units provides the required flexibility for the fabrication of metal-coordinated polymers using Co(II). Hence, the ligand 1,1′-(1,4-butanediyl)bis(benzimidazole) (L) can be used for the fabrication of Co polymers (L1, [CoL₂(H₂O)₂](NO₃)₂·8H₂O; and L2, [CoL(H₂O)₂(CH₃COO)₂]H₂O) Those polymers were obtained from the same ligand just varying slightly the synthesis conditions [18]. This variation leads to different composition and morphology for each of the polymers. While L1 forms infinite networks, the coordination of Co(II) in L2 leads to the formation of an infinite zig-zag two-dimensional polymeric structure. Furthermore, same ligand L in presence of Cd(II) ions led to the fabrication of one-dimensional helical chain polymeric structures [19].

The assembly of these structures usually is sensitive to pH values and the protonation states of the ligands, as in the case of carboxylates and nitrogen donor groups. In order to have a better understanding of the effect of the pH value on the aromatic nitrogen-donor ligands, Li et al. [12] studied the reaction system using the benzimidazole derivative H₂bic (1H-benzimidazole-5-carboxylic acid) as ligand. In this case, they used Cd(II) for the assembly of the metal-coordinated polymer. The assembly was performed at different pH values, leading to different morphologies and compositions of the polymer. Hence, at pH 5.0, a two-dimensional
supramolecular assembly consisting in stacked one-dimensional chains was obtained. However, when the pH was raised to 6.5, a rhombus network structure was obtained. Finally, at a pH of 7.2, a three-dimensional architecture based on binuclear cadmium units was retrieved.

3. Supramolecular self-assembly through $\pi-\pi$ stacking interactions

As aforementioned, coordination chemistry is not the only noncovalent interaction used for the assembly of supramolecular structures. Indeed, nanostructures can be formed through interactions such as hydrogen bond, $\pi-\pi$ stacking, metal coordination, or electrostatic interactions. In the specific case of benzimidazole derivatives, the heteroaromatic benzimidazole moiety introduces both $\pi-\pi$ attacking and coordination unit. Benzimidazole derivatives have shown gelification and formation of structures in absence of metal cations or anions and completely different structures in presence of metal cations [8, 20]. As example, N,N′-bisocyadecyl-2-(1H-benzimidazole-2-carbonyl)-l-glutamic amide, BzLG) ligand was assembled through a supramolecular gelation method named low-molecular-weight organogels (LMWGs) in various organic solvents or in water. Once the gel is formed, the solvent is removed and nanostructures can be obtained with relatively uniform structures and large quantity. BzLG gelifies in several organic solvents, including cyclohexane, toluene, acetonitrile, ethanol, and dimethyl formamide. Obtained structures relied upon the solvent used in the gelification process: from nanotubes in dimethyl formamide and acetone to nanofibers in acetonitrile and cyclohexane.

When BzLG was used to coordinate with transitional metal ions and lanthanide ions, completely different structures were obtained. Nanotube flowers were obtained upon addition of Eu(NO$_3$)$_3$ and Tb(NO$_3$)$_3$, while in the case of Cu(NO$_3$)$_2$, microflower structures were observed. The latter structures were very similar to the nanoflower structures formed from bovine serum albumin (BSA) in phosphate buffer and Cu(SO$_4$)$_2$ metal salt reported in the fabrication of protein nanoflowers and nanosponges [32, 33].

4. Benzimidazole conjugates as smart nanocontainers

The design of stimuli-responsive materials is a growing research field. These materials are capable of altering their chemical and/or physical properties upon exposure to an external stimulus, such as temperature, humidity, light, or pH. Thus, they have been applied to biomedical applications as drug delivery vectors or as degradable biocompatible containers.

The ability of benzimidazole to coordinate metal cations can be used for the detection and study of metal cations in smart biodevices and organic nanocages. Here, we show two examples, benzimidazole conjugates of cyclodextrin and calix-6-arene, in which benzimidazole units are coupled to arranged molecules that can act as containers of small molecules, releasing those molecules under specific stimuli.

4.1 Cyclodextrin conjugates

Cyclodextrins ($\beta$-CD) are cyclic biomacromolecules typically containing six to eight glucose subunits bound through $\alpha$-1,4 glycosidic bonds. They show toroid-like structures, with two external rims, one larger and the other smaller, that expose the secondary and primary hydroxyl groups of the glucose subunits, respectively. Importantly, the interior of the toroid is hydrophobic, being able to host hydrophobic molecules.
The chemical nature of benzimidazole makes it a good ligand to interact with cyclodextrin (β-CD) oligomers through hydrophobic interactions. Moreover, the physicochemical properties of benzimidazole molecules can be altered with the pH [34]. Therefore, under neutral pH condition, benzimidazole interacts with the inner part of the β-CD, blocking the diffusion through the macromolecule. As the pH is lowered, the dissociation constant between benzimidazole and β-CD decreases and benzimidazole is released to the medium. Using this approach, β-CD pH-responsive nanovalves have been fabricated: as the pH decreases, the external rings are opened, and the cargo release occurs. More complex structures were designed for sensing glucose or lactose using this system [35, 36].

4.1.1 Assembly into cyclodextrin-like architectures

The versatility and the high ability of benzimidazole derivatives to assemble are here demonstrated [4–6]. Through the controlled coordination to metal cations, that is, Pd(II), it is possible to self-assemble macrocyclic containers that mimic β-CD [21]. Moreover, these nanocontainers have the ability to bind anion guests and induce the transformation in the morphology and compositional unit of the nanocontainer. The hydrogen bonding between the inner surface of the macrocycles and the bound guests induced the fit—transformation properties of the assembled material, as observed in nature. Hence, the in situ anion-adaptative self-assembly gives rise to PdₙL₂ₙ species for n:3, 6, 7. As example, Sun et al. demonstrated the assembly of BzI-based ligands using square-planar palladium(II) ions into well-defined hydrogen-bonding pockets that will find applications in molecular sensing and catalysis.

4.2 Calix-6-arene conjugates

The benefits of the combination of benzimidazole molecules with nanocontainer scaffolds are also evidenced in this example in which benzimidazole is attached to calix-6-arenes [22]. Calix-6-arenes are organic macrocycles composed of (derivatives of) phenol subunits. Due to its hydrophobic cavity, they can be used to host smaller hydrophobic molecules or ions. They have been extensively used as a molecular platform to host catalytic units.

In benzimidazole-calixarene conjugates, the benzimidazole moieties are localized hanging out from the small rim of the macrocycle, pointing toward the environment. The coordination of metal cations to the imidazole ring of the benzimidazole molecule mimics the hydrophobic environment of the copper site in proteins and enzymes [37, 38]. The coordination of metal cations, that is, Cu(II), triggers a detectable modification in the structure of the conjugate, therefore being this a very sensitive method for the detection of metal ions.

5. Recent applications of assembled materials and new perspectives

As aforementioned, the assembly of benzimidazole and its derivatives has been utilized for the fabrication of stable materials with applications in several fields [39–42], some of them collected in Table 1: sensor fabrication [22], drug delivery systems [35], fuel cell design, biomedicine [43], conductivity in liquid crystals [23], or the fabrication of nanostructures [17].

Additionally, new applications of benzimidazole-derived materials are being raised. Thanks to the intrinsic properties of polymeric structures and the optical properties of some of the macroassemblies described above (luminescence, phosphorescence, or fluorescence), there is a growing interest in using these structures
as healable and/or writable materials. These polymeric assemblies respond to external stimuli, for example, heat, presence of ions, with the surface rearrangement, and entanglement of the chains. The use of benzimidazole moieties in these systems, thanks to their chromophore rings, allows the use of an optical irradiation to heal the material [24]. Moreover, the ability of these polymers to bind and interact with different anions shows that their optical properties are used for advanced application in data recording and security protection [44].

6. Conclusions

In this chapter, we show the use of benzimidazole and its derivatives as important ligands that are currently being used for their supramolecular assembly into large structures with interesting properties and applications. Due to the physicochemical properties of benzimidazole, different chemistries and interactions can guide the assembly into very stable materials. Among them, the metal coordination to the imidazole ring seems to be the most exploited one for the formation of metal macro molecules, metal coordination polymers, and metal-organic frameworks. The selected benzimidazole derivatives and metal cation, together with the utilized synthesis conditions, will lead to the formation of materials with very diverse size and morphology. Thus, the establishment of a solid knowledge on the prediction of the assembled structures would contribute to the advancement of material science with strong strategic implications for the on-demand synthesis of smart responsive materials. However, in spite of the large efforts that are being done, currently there is no method to predict the composition and structure of the eventually synthesized materials.

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