Photoluminescent Coordination Polymers Based on Group 12 Metals and 1H-Indazole-6-Carboxylic Acid

Antonio A. García-Valdivia 1,*, Estitxu Echenique-Errandonea 2,*, Gloria B. Ramírez-Rodríguez 1,*, José M. Delgado-López 1,*, Belén Fernández 3,*, Sara Rojas 1,*, Javier Cepeda 2,*, and Antonio Rodríguez-Díezeguez 1,*

1. Introduction

The study of coordination polymers (CPs) and metal-organic frameworks (MOFs) is at the forefront of modern inorganic chemistry due to their broad range of potential applications, spanning from magnetism and luminescence, through catalysis and sensing, to gas separation and storage, and biomedicine [1,2]. Through an adequate selection of their building blocks (metal ions and organic ligands), CPs and MOFs can be designed to enhance a particular property [3–5]. It is well known that nitrogen-containing heterocycles are molecules commonly employed as ligands owing to not only their good coordination ability, but also pharmacological relevance, given that they are important scaffolds widely present in numerous commercially available drugs [6]. The most famous are diazepam, isoniazid, chlorpromazine, metronidazole, barbituric acid, captopril, chloroquine, azidothymidine and anti-pyrimine. As a result of their diverse biological activities, nitrogen heterocyclic compounds have always been attractive targets to develop new active compounds. This is the case for 1H-indazole-6-carboxylic acid (H2L), a common moiety in the pharmaceutical industry [7]. Polysubstituted indazole-containing compounds furnished with different functional groups usually present significant pharmacological activities and serve as structural motifs in drug molecules (i.e., nirparib-anticancer drug, pazopanib-approved by the FDA for renal cell carcinoma, bendazac and benzydamine-antiinflammatory
drugs) [8]. From the structural point of view, indazole is an aromatic heterocyclic molecule with a benzene ring fused to a pyrazole ring [9]. It shows three tautomeric forms (Scheme 1) being tautomer A favoured over B and C due to its higher degree of aromaticity [10].

\[ \text{1H-indazole} \leftrightarrow \text{2H-indazole} \leftrightarrow \text{3H-indazole} \]

**Scheme 1.** Indazole tautomerism (A, B, and C from left to right).

H\(_2\)L is presented here as an ideal candidate to form CPs or MOFs as it possesses multiple coordination possibilities, not only derived from its carboxylate group, but also from its pyrazole function. Thus, a great variety of coordination modes are possible, according to similar ligands containing carboxylate and pyrazole chemical functions in crystallized complexes (Scheme 2). Until now, only one complex based on this ligand has been reported so far [11]. In that work, Kruger et al. described in detail four substituted indazole derivatives containing pyridine or carboxylic functionalities upon coordination with Cu(II) ions in solution and solid state. In the complex, 1\(H\)-indazole-6-carboxylate acts as a bridging ligand showing a tridentate coordination mode: the carboxylate group coordinates to two Cu(II) atoms in a syn,syn mode to establish a dimeric paddle-wheel shaped entity, whereas the non-protonated nitrogen atom of the pyrazole ring links to a third Cu(II) atom in a monodentate way (see the highlighted modes in Scheme 2). Aside from this work mainly focused on the description of a new compound, it should be pointed out that some Co(II)-based complexes with indazole derivatives have shown a capacity to bind to DNA [12].

**Scheme 2.** Possible coordination modes of 1\(H\)-indazole-6-carboxylate ligand. Note that only those two modes highlighted in black have been described in bibliography whereas the rest correspond to potential binding modes.
On the other hand, H$_2$L may also present interesting photoluminescence (PL) properties due to its aromatic nature and the presence of carboxylic groups, with potentially strong light absorption [13]. When these indazole-carboxylate ligands are coordinated to metal centres in the crystal structure of a CP, PL tends to be enhanced by means of the well-known crystal-induced luminescence effect [14]. Among others, metal ions from group 12 are particularly appropriate for their use in PL as they present a closed-shell electronic configuration in which d-d transitions cannot occur [15,16]. In fact, many CPs and MOFs formed by these metal ions have been reported during the last decade [17,18], some of which present not only strong and bright fluorescent emissions, but also long-lived phosphorescence that may be traced by the naked eye [19–21]. Moreover, the presence of these ions may also promote ligand-to-metal charge transfer (LMCT) as metal ions possess empty orbitals that can be populated in the excited state, and therefore the PL emission may be modulated with regard to the ligand-centred (LC) emissions [22,23]. Irrespective of the luminescence mechanism occurring in these systems, the interest for group 12-based compounds has increased given their potential application as not only lighting devices, but also as luminescence-based molecular detectors [24], thermometers [25] and anti-counterfeiting inks, among others [26]. Particularly for indazole derivatives playing as ligands, many Zn-/Cd-indazole complexes have already proved efficient luminescent CPs under UV irradiation [27].

Considering all the above, in this work we present the synthesis, structural characterisation and PL properties of two new coordination polymers based on group 12 metals and 1H-indazole-6-carboxylic acid of general formula [Zn(L)(H$_2$O)]$_n$ (1) and [Cd$_2$(HL)$_4$]$_n$ (2). Their emission characteristics have been studied both from the theoretical and experimental points of view, involving the measurements in the solid state as well as in aqueous medium.

2. Results and Discussion

The reaction of 1H-indazole-6-carboxylic acid gave rise to two compounds based on group 12 metals which exhibit a different structural dimensionality. In particular, the solvothermal reaction of the 1H-indazole-6-carboxylic acid ligand with zinc acetate salt (Zn(CH$_3$COO)$_2$) using a 1:2 molar ratio in a N,N-dimethylformamide/water (DMF/H$_2$O) mixture afforded a 1D CP, namely 1 (see Experimental Section for further details). Similarly, the use of cadmium acetate salt (Cd(CH$_3$COO)$_2$) salt in the synthesis, successfully led to a 3D MOF, namely 2. This fact can be explained by the larger ion size of Cd(II), which may admit higher coordination numbers, involving the participation of additional ligands and increasing the metal-to-ligand connectivity.

2.1. Description of the Structures

2.1.1. Structural Description of [Zn(L)(H$_2$O)]$_n$ (1)

Compound 1 crystallizes in the $P2_1/n$ space group and consists of a double chain structure in which Zn(II) ions are bridged by nitrogen atoms of L$^{2-}$ in a bidentate way, giving rise to a stable and in plane Zn$_2$N$_4$ dimeric core as a six membered ring (Figure 1).

![Figure 1. Representation of the 1D polymeric chain in which Zn$_2$N$_4$ planar six membered ring is observed (zinc, nitrogen, oxygen, and carbon are represented in green, blue, red, and grey, respectively; hydrogen atoms are omitted for clarity).](image-url)
The Zn(II) ion is also coordinated to a carboxylate moiety of the indazole derivative ligand in a monodentate way, which extends the dimeric entity into infinite 1D chains running along the crystallographic [100] direction. The coordination sphere of Zn is completed by the coordination of a water molecule (see Table S1 in the ESI for further information about bond lengths and angles). The ZnN₂O₂ coordination sphere can be described as a tetrahedron, although Zn ions show a geometry close to an axially vacant trigonal bipyramid according to continuous-shape-measures (CShMs) using SHAPE software (Tables S2 and S3, in the ESI) [28].

The packing of the double chains is ruled by intermolecular interactions, among which hydrogen bonding interactions established between coordination water molecules and carboxylate oxygen atoms are to be highlighted (Figure 2). In particular, the coordinated water molecule is involved in hydrogen bonding interactions in which non-coordinated carboxylate oxygen atoms belonging to adjacent chains act as receptors. Additionally, the angle formed among neighbouring chains allows for the formation of C–H···π interactions between aromatic rings, reinforcing the stability of the supramolecular crystal building (see Figure S5 in the ESI).

![Figure 2](image_url)

**Figure 2.** Perspective view of the chains of [Zn(L)(H₂O)]ₙ packed in the framework (hydrogen atoms have been omitted for clarity).

2.1.2. Structural Description of [Cd₂(HL)₄]ₙ (2)

Compound 2 crystallizes in the triclinic P-1 space group. The asymmetric unit contains two non-equivalent Cd(II) atoms and four ligand molecules. Each Cd(II) ion is connected to two monodentate indazole nitrogen atoms and four oxygen atoms of the carboxylate group of the ligand. Cd1 and Cd2 ions are doubly linked by ancillary syn-anti carboxylate moieties of 1-H-indazole-6-carboxylate ligands (namely A, C and D). However, the carboxylate group of B ligand presents a different coordination pattern, in which O1B connects in a monodentate way to both Cd1 and Cd2 atoms giving rise to alternating five and six membered rings (Figure 3, see also the view along b axis in Figure S6 in the ESI), whereas O2B atom remains unconnected to any metal centre.
CShMs indicate that different ligand coordination modes affect the connectivity of the metal centres, which leads to the formation of a distinct crystal structure. When comparing 1 and 2 compounds, the coordination spheres of Cd1 and Cd2 are described as octahedra according to SHAPE measurements (Tables S2 and S3 in the SI). M···N2 distances are slightly shorter than in compound 1 (in the 1.969 and 2.293–2.316 Å ranges, respectively), similarly to the M···O1carboxylate bond distances (between 1.935 and 2.320 Å, see Table S1 in the ESI). As a result, a 3D framework is obtained in the case of 2 by the further linkage of the carboxylate groups to Cd(II) atoms along a metal-carboxylate rod (Figure 4). Considering the connectivity of the metal ions and HL ligands, this framework may be described as a 5,6T24 topological network with the \((3^2.4^2.5^2.6^2.7^2)(3^2.4^4.5^4.6^2.7^3)\) point symbol, as previously observed in the MOF of \([\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_2(\text{C}_{10}\text{O}_8\text{H}_2)]\) or MIL-118A [29].

**Figure 3.** View of the coordination of Cd(II) ions to HL in compound 2 (cadmium, nitrogen, oxygen, and carbon are represented in dark-yellow, blue, red, and grey, respectively; hydrogen atoms have been omitted for clarity).

**Figure 4.** Perspective of 3D structure of compound 2 (hydrogen atoms have been omitted for clarity).
To end up with the structural description, it is worth mentioning that compound 2 presents some remarkable supramolecular interactions that reinforce its packing. Unlike with hydrogen bonding and C–H⋯π interactions governing the crystal structure of 1, 2 contains π⋯π stacking interactions. In particular, the aromatic rings of HL promote strong face-to-face contacts among the whole structure (see Figure S5 in the ESI).

2.2. Fourier Transformed Infrared (FTIR) Spectroscopy

The analysis of the FTIR spectra of 1 and 2 confirms the coordination of zinc(II) and cadmium(II) ions to the N-containing carboxylate ligand (Figure S1, see the ESI). FTIR spectra of both compounds confirmed a shift in the wavelengths in comparison to the pure linker, suggesting the formation of interactions between the linker and the metals. The main vibrations of 1H-indazole-6-carboxylic acid associated with the U_{C=N} stretching vibration at 1633 cm\(^{-1}\), and the asymmetric and symmetric vibrations of the carboxylate groups at 1683 and 1423 cm\(^{-1}\) are shifted when compared with the spectra of 1 and 2. The bands found at 1537 and 1589 cm\(^{-1}\) for complex 1 and 2, respectively, are attributed to the U_{C=N} stretching vibration of the indazole ring [30]. Moreover, the strong absorption peak observed at 1558 and 1402 cm\(^{-1}\) for 1, and 1541 and 1411 cm\(^{-1}\) for 2, respectively, revealed the asymmetric and symmetric vibrations of the carboxylic groups [31]. Finally, the strong broad band in the range of 3317–3086 cm\(^{-1}\) was assigned to the O–H stretching vibration of the coordinated water molecule in complex 1 [32].

2.3. Luminescence Properties

As previously mentioned, complexes consisting of metal ions with d\(^{10}\) electronic configuration are known to yield strong PL emissions. The completely filled d-orbitals disable ligand field d–d transitions, eliminating fluorescence quenching and allowing the occurrence of PL [14]. Thus, the development of d\(^{10}\)-based compounds is interesting for photochemical, electroluminescence and sensing applications [17,33]. The extended aromaticity of the 1H-indazole-6-carboxylate ligand coordinated to Zn(II) and Cd(II) atoms suggests the existence of emissive properties of 1 and 2. The emission of these compounds are found to be similar to ligand emission, which may stem from the ligand-centred π–π* electronic transitions, as shown in Figure 5. Consequently, it can be suggested that the highly conjugated 1H-indazole-6-carboxylate ligand is the main part contributing to the emission [34]. An intense broad band at 350–450 nm dominates the emission spectra of all compounds upon 325 nm excitation (in view of the maxima found in the excitation spectra), among which the maxima at 362 and 388 nm, 363 and 381 nm, and 363 and 391 nm can be distinguished for the ligand, and compounds 1 and 2, respectively; which impues all compounds with blue emission. The similar emission band of 2 and the free ligand must be attributed to the fact that 2 possesses the protonated form of the ligand (HL\(^{-}\)) whereas it is completely deprotonated (L\(^{2-}\)) in 1. In a comparative scale, the ligand spectrum shows two well-defined maxima (not that easily identified for the compounds) and relatively higher intensity (Figure S2, SI). It is worth noticing that the observed luminescence resembles to that shown by other previously reported CPs containing other isomers of indazole-carboxylates [35,36].
can be distinguished for the ligand, and compounds 1 and 2, respectively; which imbues all compounds with blue emission. The similar emission band of 2 and the free ligand must be attributed to the fact that 2 possesses the protonated form of the ligand (HL$^{-}$) whereas it is completely deprotonated (L$^{2-}$) in 1. In a comparative scale, the ligand spectrum shows two well-defined maxima (not that easily identified for the compounds) and relatively higher intensity (Figure S2, SI). It is worth noticing that the observed luminescence resembles to that shown by other previously reported CPs containing other isomers of indazole-carboxylates [35,36].

In order to get a deeper insight into the emission mechanism, TD-DFT calculations were performed on suitable models of compounds 1 and 2. The calculated spectra reproduce fairly well the experimental ones, indicating that the process is driven by singlet transitions occurring between the molecular orbitals shown in Figure 5. In both cases, the electron density in HOMO orbitals, HOMO-2 and HOMO-4 for compound 1 and 2, respectively, extend over the bonds over the whole ligand molecule (signifying a π orbital) whereas LUMO orbitals, LUMO+2 and LUMO+1 for compound 1 and 2, respectively, feature a π$^*$ character. Therefore, it can be stated that the transitions involved in the photoluminescence of compound 1 and 2 are mainly of π$^*$ ← π nature induced by ligand centred emission.

Inspired by the potential biomedical properties of the ligand on the basis of its similar structure to other indazole derivatives [7,8], we studied the stability and fluorescence
Inorganics 2021, 9, 20

3. Materials and Methods

3.1. Materials and Physical Measurements

All the reagents were purchased commercially and used without any previous purification. Elemental analysis (C, H and N) were carried out at the Centro de Instrumentación Científica (University of Granada) on a Fisons-Carlo Erba analyzer model EA 1108 (Thermo Scientific, Waltham, MA, USA). FTIR spectra (400–4000 cm⁻¹) were recorded on a Nicolet FT-IR 6700 spectrometer (Thermo Scientific, Madrid, Spain) in KBr pellets.

3.2. Synthesis of [Zn(L)(H₂O)]ₙ (1)

0.010 g (0.006 mmol) of 1H-indazole-6-carboxylic acid (H₂L) was dissolved in 0.5 mL of DMF. Then, 0.5 mL of water was added to the ligand solution. In a separate vial, 0.0134 g (0.03 mmol) of Zn(CH₃COO)₂ was dissolved in 0.5 mL of water. Similarly, once metal salt was dissolved, 0.5 mL DMF were added to the solution. Metal solution was added dropwise to the ligand solution, and the resulting colourless mixture was placed in a closed glass vessel and heated in an oven at 100 °C for 24 h. X-ray quality crystals of 1 were obtained during heating process under autogenous pressure and washed with water. Yield: 64% based on Zn. Anal Calcd. for C₈H₄N₂O₃Zn: C, 39.46; H, 2.48; N, 11.50. Found: C, 39.39; H, 2.41; N, 11.59. In addition to the elemental analyses, the purity of all the samples was checked by FT-IR spectra.

3.3. Synthesis of [Cd₂(HL)₄]ₙ (2)

The same synthetic procedure was carried out to obtain complex 2, by replacing Zn(CH₃COO)₂ by 0.01651 g (0.03 mmol) of Cd(CH₃COO)₂. X-ray quality crystals were obtained and washed with water. Yield: 54% based on Cd. Anal Calcd. for C₃₂H₂₀Cd₂N₈O₈: C, 44.21; H, 2.32; N, 12.89. Found: C, 44.16; H, 2.29; N, 12.91. In addition to the elemental analyses, the purity of all the samples was checked by FT-IR spectra.

3.4. Crystallographic Refinement and Structure Solution

Single crystals of suitable dimensions were used for data collection. For compound 1 and 2, diffraction intensities were recorded on a Bruker X8 APEX II and Bruker D8 Venture with a Photon detector (Bruker, Madrid, Spain) equipped with graphite monochromated MoKα radiation (λ = 0.71073 Å). The data reduction was performed with the APEX2 software [38] and corrected for absorption using SADABS [39]. In all cases, the structures were solved by direct methods and refined by full-matrix least-squares with SHELXL-2018 [40]. The main refinement parameters are listed in Table 1. Details of selected bond
lengths and angles are given in Table S2 in the ESI. CCDC reference numbers for the structures are 1,948,382 and 1,948,383 for Cd and Zn coordination polymers, respectively.

| Compound | 1 | 2 |
|----------|---|---|
| Formula  | C₈H₆N₂O₃Zn | C₃₂H₂₀Cd₂N₈O₈ |
| Mᵣ (g mol⁻¹) | 243.52 | 869.36 |
| Crystal system | monoclinic | triclinic |
| Space group | P₂₁/n | P–1 |
| Temperature (K) | 100 (2) | 100 (2) |
| a (Å) | 9.774 (3) | 8.7080 (4) |
| b (Å) | 5.7633 (15) | 9.0640 (3) |
| c (Å) | 14.592 (4) | 19.4510 (7) |
| α (°) | 90 | 101.089 (1) |
| β (°) | 95.626 (7) | 90.961 (2) |
| γ (°) | 90 | 98.063 (1) |
| V (Å³) | 818.0 (4) | 1490.18 (1) |
| Z | 4 | 2 |
| ρ (g cm⁻³) | 1.977 | 1.937 |
| µ (mm⁻¹) | 2.979 | 1.497 |
| Unique reflections | 1035 (817) | 7671 (5938) |
| Rint | 0.1342 | 0.0722 |
| GoF a | 1.082 | 1.107 |
| R¹ b /wR² c [I>2σ(I)] | 0.0777/0.0535 | 0.0604/0.0352 |
| R¹ b /wR² c [all data] | 0.1075/0.0994 | 0.0823/0.0672 |

Largest difference in peak and hole (e Å⁻³) | 0.635 and −0.0656 | 1.062 and −1.046 |

³ R₁ = S[|Fₒ| − |Fᵣ|] / S|Fₒ|. ⁴ wR² = S[w(Fₒ² − Fᵣ²)²] / S[w(Fₒ²)²] ½; where w = 1/[σ²(Fₒ²) + (aP)² + bP] and P = (max(Fₒ,0) + 2Fᵣ²)/3 with a = 0.0.0319 (1), 0.0380 (2) and b = 6.9969 (1).

3.5. Photophysical Measurements

UV-Vis absorption spectra were recorded on UV-2600 UV/vis Shimadzu spectrophotometer using polycrystalline samples of compounds 1 and 2. PL measurements were carried out on crystalline samples at room temperature using a Varian Cary-Eclipse fluorescence spectrophotometer equipped with a Xe discharge lamp (peak power equivalent to 75 kW), Czerny–Turner monochromators, and an R-928 photomultiplier tube. For the fluorescence measurements, the photomultiplier detector voltage was fixed at 600 V, and the excitation and emission slits were set at 5 and 2.5 nm, respectively. Phosphorescence spectra were recorded with a total decay time of 20 ms, delay time of 0.2 ms and gate time of 5.0 ms. The photomultiplier detector voltage was set at 800 V, and both excitation and emission slits were open to 10 nm.

4. Conclusions

The reaction between 1H-indazole-6-carboxylic acid ligand and Zn(II) or Cd(II) leads the formation of two new coordination polymers with different dimensionalities. Compound 1 possesses a double chain structure, whereas compound 2 exhibits a 3D structure. Emissive properties of both complexes have been studied demonstrating that their photoluminescent emission is driven by the ligand centred π*←π transition. The similar luminescent properties between compound 2 and the linker may be consequence of the partially protonated HL⁻ ligand present in 2. This work is pioneer in studying and comparing the luminescent properties of 1H-indazole-6-carboxylic acid (H₂L) and its complexes, which represent a common moiety in pharmaceutical industry. In this regard, novel materials based on this ligand are being developed in our laboratory using lanthanide ions to enhance their luminescent properties.
Supplementary Materials: The following are available online at https://www.mdpi.com/2304-6740/9/3/20/s1, Figure S1: Infrared spectra of the ligand and compounds 1 and 2, Figure S2: Emission spectra of the ligand and compounds 1 and 2 under λexc = 325 nm, Figure S3: Excitation spectra of compounds monitored at the emission maxima: (a) λem = 381 nm for 1 and (b) λem = 391 nm for 2, Figure S4: Comparative view of the absorption spectra of compounds (a) 1 and (b) 2 in solid state and aqueous solution, Figure S5: The most representative intermolecular interactions and packing modes for complexes 1 (up) and 2 (down). H bonds, π⋯π and C–H⋯π interactions are shown with dashed blue, green and orange lines, respectively, Figure S6: View along a (left), b (middle) and c (right) axis of complex 1 (up) and 2 (down), Figure S7: UV-Vis spectra of compounds (a) 1 and (b) 2 in aqueous solutions acquired at times (0 h and after 24 h), Table S1: Selected bond lengths (Å) and angles (°) for complexes 1 and 2, Table S2: Continuous Shape Measurements for the ZnN2O2 coordination environment, Table S3: Continuous Shape Measurements for the CdN2O2 coordination environment. The CIF and the checkCIF output files are included in the Supplementary Materials.

Author Contributions: Conceptualization, A.R.-D.; methodology, A.A.G.-V. and E.E.-E.; software, J.C.; validation, J.M.D.-L. and S.R.; formal analysis, B.F. and S.R.; investigation, A.A.G.-V. and G.B.R.-R.; resources, B.F. and A.R.-D.; data curation, G.B.R.-R. and J.C.; writing—original draft preparation, E.E.-E.; writing—review and editing, J.C. and A.R.-D.; visualization, B.F.; supervision, A.R.-D.; project administration, J.C. and A.R.-D.; funding acquisition J.C. and A.R.-D. All authors have read and agreed to the published version of the manuscript.

Funding: Financial support was given by Junta de Andalucía (Spain) (FQM-394), University of the Basque Country (GIU 17/13), Gobierno Vasco/Eusko Jaurlaritza (IT1005-16), and the Spanish Ministry of Science, Innovation and Universities (MCIU/AEI/FEDER, UE) (PGC2018-102052-A-C22, PGC2018-102052-B-C21). J.M.D.L. and G.B.R.R. acknowledge the FEDER/MCIU/AEI for their Ramón y Cajal (RYC-2016-21042) and Juan de la Cierva (JdC-2017) fellowships, respectively. S.R. acknowledges the Juan de la Cierva Incorporacion Fellowship (grant agreement nº. IJC2019-038894-I). E.E.-E. is grateful to the Government of the Basque Country for the predoctoral fellowship. The authors thank for technical and human support provided by SGIker of UPV/EHU and European funding (ERDF and ESF).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

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

References
1. McKinlay, A.C.; Morris, R.E.; Horcajada, P.; Férey, G.; Gref, R.; Couvreur, P.; Serre, C. BioMOFs: Metal-organic frameworks for biological and medical applications. Angew. Chem. Int. Ed. 2010, 49, 6260–6266. [CrossRef]
2. Tranchemontagne, D.J.; Tranchemontagne, J.L.; O’keeffe, M.; Yaghi, O.M. Secondary building units, nets and bonding in the chemistry of metal–organic frameworks. Chem. Soc. Rev. 2009, 38, 1257–1283. [CrossRef] [PubMed]
3. Zhang, Q.; Cui, Y.; Qian, G. Goal-directed design of metal–organic frameworks for liquid-phase adsorption and separation. Coord. Chem. Rev. 2019, 378, 310–332. [CrossRef]
4. Bünzli, J.-C.G. On the design of highly luminescent lanthanide complexes. Coord. Chem. Rev. 2015, 293–294, 19–47. [CrossRef]
5. Chen, C.T.; Suslick, K.S. One-dimensional coordination polymers: Applications to material science. Coord. Chem. Rev. 1993, 128, 293–322. [CrossRef]
6. Heravi, M.M.; Zadsirjan, V. Prescribed drugs containing nitrogen heterocycles: An overview. RSC Adv. 2020, 10, 44247–44311. [CrossRef]
7. Horton, D.A.; Bourne, G.T.; Smythe, M.L. The combinatorial synthesis of bicyclic privileged structures or privileged substructures. Chem. Rev. 2003, 103, 893–930. [CrossRef]
8. Zhang, S.G.; Liang, C.G.; Zhang, W.H. Recent advances in indazole-containing derivatives: Synthesis and biological perspectives. Molecules 2018, 23, 2783. [CrossRef]
9. Dong, J.; Zhang, Q.; Wang, Z.; Huang, G.; Li, S. Recent Advances in the Development of Indazole-based Anticancer Agents. ChemMedChem 2018, 13, 1490–1507. [CrossRef]
10. Büchel, G.E.; Kossatz, S.; Sadique, A.; Rapta, P.; Zalibera, M.; Bucinski, L.; Komorovský, S.; Telser, J.; Eppinger, J.; Reiner, T. et al. Cis-Tetrachlorido-dis(indazole)osmium(IV) and its osmium(III) analogues: Paving the way towards the cis-isomer of the ruthenium anticancer drugs KP1019 and/or NKPI339. Dalt. Trans. 2017, 46, 11925–11941. [CrossRef]
11. Hawes, C.S.; Kruger, P.E. Discrete and polymeric Cu(ii) complexes featuring substituted indazole ligands: Their synthesis and structural chemistry. Dalt. Trans. 2014, 43, 16450–16458. [CrossRef]
12. Long, B.F.; Huang, Q.; Wang, S.L.; Mi, Y.; Wang, M.F.; Xiong, T.; Zhang, S.C.; Yin, X.H.; Hu, F.L. Five new cobalt(II) complexes based on indazole derivatives: Synthesis, DNA binding and molecular docking study. *J. Coord. Chem.* 2019, 72, 645–663. [CrossRef]

13. Furman, J.D.; Burwood, R.P.; Tang, M.; Mikhailovsky, A.A.; Cheetham, A.K. Understanding ligand-centred photoluminescence through flexibility and bonding of anthraquinone inorganic-organic frameworks. *J. Mater. Chem.* 2011, 21, 6595–6601. [CrossRef]

14. Yuan, W.Z.; Shen, X.Y.; Zhao, H.; Lam, J.W.Y.; Tang, L.; Lu, P.; Wang, C.; Liu, Y.; Wang, Z.; Zheng, Q.; et al. Crystallization-induced phosphorescence of pure organic luminogens at room temperature. *J. Phys. Chem. C* 2010, 114, 6090–6099. [CrossRef]

15. Cepeda, J.; Rodríguez-Díezquez, A. Tuning the luminescence performance of metal-organic frameworks based on d10 metals: From an inherent versatile behaviour to their response to external stimuli. *CrystEngComm* 2016, 18, 8556–8573. [CrossRef]

16. Solov’ev, K.N.; Borisovich, E.A. Intramolecular heavy-atom effect in the photophysics of organic molecules. *Phys. Uspekhi* 2005, 48, 231–253. [CrossRef]

17. Seco, J.M.; Pérez-Yáñez, S.; Briones, D.; García, J.A.; Cepeda, J.; Rodríguez-Díezquez, A. Combining Polycarboxylate and Bipyridyl-like Ligands in the Design of Luminescent Zinc and Cadmium Based Metal-Organic Frameworks. *Cryst. Growth Des.* 2017, 17, 3893–3906. [CrossRef]

18. Cepeda, J.; Pérez-Yáñez, S.; Rodríguez-Díezquez, A. Luminescent Zn/Cd-based MOFS, CPS and their applications. In *Advances in Materials Science Research*, Wythers, M.C., Ed.; Nova Science Publishers: Hauppauge, NY, USA, 2017; Volume 28, ISBN 9781536109054.

19. San Sebastián, E.; Rodríguez-Díezquez, A.; Seco, J.M.; Cepeda, J. Coordination Polymers with Intriguing Photoluminescence Behavior: The Promising Avenue for Greatest Long-Lasting Phosphors. *Eur. J. Inorg. Chem.* 2018, 2155–2174. [CrossRef]

20. Pajuelo-Corral, O.; Rodríguez-Díezquez, A.; García, J.A.; San Sebastián, E.; Seco, J.M.; Cepeda, J. Chiral coordination polymers based on d10 metals and 2-aminoanocinate with blue fluorescent/green phosphorescent anisotropic emissions. *Dalt. Trans.* 2018, 47, 8746–8754. [CrossRef]

21. Yang, Y.; Wang, K.Z.; Yan, D. Ultralong Persistent Room Temperature Phosphorescence of Metal Coordination Polymers Exhibiting Reversible pH-Responsive Emission. *ACS Appl. Mater. Interfaces* 2016, 8, 15489–15496. [CrossRef]

22. Liu, Q.; Wang, R.; Wang, S. Blue phosphorescent Zn(II) and orange phosphorescent Pt(II) complexes of 4,4′-dimethyl-6′,6′-dimethyl-2′,2′-bipyrimidine. *Dalt. Trans.* 2004, 35, 2073–2079. [CrossRef]

23. Barbieri, A.; Accorsi, G.; Armaroli, N. Luminescent complexes beyond the platinum group: The d10 avenue. *Chem. Commun.* 2008, 2185–2193. [CrossRef]

24. Hu, Z.; Deibert, B.J.; Li, J. Luminescent metal-organic frameworks for chemical sensing and explosive detection. *Chem. Soc. Rev.* 2014, 43, 5815–5840. [CrossRef] [PubMed] [CrossRef]

25. Leo, P.; Briones, D.; García, J.A.; Cepeda, J.; Orcajo, G.; Calleja, G.; Rodríguez-Díezquez, A.; Martínez, F. Strontium-Based MOFs Showing Dual Emission: Luminescence Thermometers and Toluene Sensors. *Inorg. Chem.* 2020, 59, 18432–18443. [CrossRef]

26. Liu, J.; Zhuang, Y.; Wang, L.; Zhou, T.; Hiroaki, N.; Xie, R.-J. Achieving Multicolor Long-Lived Luminescence in Dye-Encapsulated Metal–Organic Frameworks and Its Application to Anticounterfeiting Stamps. *ACS Appl. Mater. Interfaces* 2018, 10, 1802–1809. [CrossRef]

27. Sun, Y.-X.; Sun, W.-Y. Zinc(ii)– and cadmium(ii)–organic frameworks with 1-imidazole-containing and 1-imidazole-carboxylate ligands. *CrystEngComm* 2015, 17, 4045–4063. [CrossRef]

28. Alvarez, S.; Avenir, D.; Lunnell, M.; Pinsky, M. Continuous symmetry maps and shape classification. The case of six-coordinated metal compounds. *New J. Chem.* 2006, 26, 996–1009. [CrossRef]

29. Volkering, C.; Loiseau, T.; Guillou, N.; Ferey, G.; Haouas, M.; Taulelle, F.; Audebrand, N.; Margiolaki, I.; Popov, D.; Burghammer, M.; et al. Structural transitions and flexibility during dehydration—Rehydration process in the MOF-type aluminium pyromellitate A12(OH)2[C1008H2](MIL-118). *Cryst. Growth Des.* 2009, 9, 2927–2936. [CrossRef]

30. Boča, M.; Baran, P.; Boča, R.; Fuess, H.; Kickelbick, G.; Linert, W.; Renz, F.; Svoboda, I. Selective imidazolidine ring opening during complex formation of iron(III), copper(II), and zinc(II) with a multidentate ligand obtained from 2-pyridinecarboxaldehyde N-oxide and triethylenetetramine. *Inorg. Chem.* 2000, 39, 3205–3212. [CrossRef]

31. Xiao, H.; Li, X.B.; Qin, G.F.; Xia, Y.; Zhou, G. Directed assembly of cobalt(II) 1-H-indazole-3-carboxylic acid coordination networks by bipyridine and its derivatives: Structural versatility, electrochemical properties, and antifungal activity. *J. Iran. Chem. Soc.* 2016, 13, 793–802. [CrossRef]

32. Ohno, K.; Okumura, M.; Akai, N.; Katsumoto, Y. The effect of cooperative hydrogen bonding on the OH stretching-band shift for water clusters studied by matrix-isolation infrared spectroscopy and density functional theory. *Phys. Chem. Chem. Phys.* 2005, 7, 3005–3014. [CrossRef] [PubMed]

33. Salinas-Castillo, A.; Calahorro, A.J.; Briones, D.; Fairen-Jiménez, D.; Gándara, F.; Mendicute-Fierro, C.; Seco, J.M.; Pérez-Mendoza, M.; Fernández, B.; Rodríguez-Díezquez, A. 2D-cadmium MOF and gismondine-like zinc coordination network based on the N-(2-tetrazolethyl)-4′-glycine linker. *New J. Chem.* 2015, 39, 3982–3986. [CrossRef]

34. Pamei, M.; Puzari, A. Luminescent transition metal–organic frameworks: An emerging sensor for detecting biologically essential metal ions. *Nano-Struct. Nano-Objects* 2019, 19, 100364. [CrossRef]

35. García-Valdivia, A.A.; Zabala-Lekuona, A.; Ramírez-Rodríguez, G.B.; Delgado-López, J.M.; Fernández, B.; Cepeda, J.; Rodríguez-Díezquez, A. 2D-Coordination polymers based on 1H-indazole-4-carboxylic acid and transition metal ions: Magnetic[,] luminescence and biological properties. *CrystEngComm* 2020, 22, 5086–5095. [CrossRef]
36. García-Valdivia, A.A.; Pérez-Mendoza, M.; Choquesillo-Lazarte, D.; Cepeda, J.; Fernández, B.; Souto, M.; González-Tejero, M.; García, J.A.; Espallargas, G.M.; Rodríguez-Díéguez, A. Interpenetrated Luminescent Metal–Organic Frameworks based on 1H-Indazole-5-carboxylic Acid. *Cryst. Growth Des.* **2020**, *20*, 4550–4560. [CrossRef]

37. Dobretsov, G.E.; Syrejschikova, T.I.; Smolina, N.V. On mechanisms of fluorescence quenching by water. *Biophysics* **2014**, *59*, 183–188. [CrossRef]

38. Bruker Apex2. *B.A.I. Bruker Apex2; Bruker AXS Inc.: Madison, WI, USA*, 2004.

39. Sheldrick, G.M. SADABS 1996, Program for Empirical Adsorption Correction. Available online: [https://cmacd.myweb.cs.uwindsor.ca/Teaching/553-class/sadabs.pdf](https://cmacd.myweb.cs.uwindsor.ca/Teaching/553-class/sadabs.pdf) (accessed on 16 January 2021).

40. Sheldrick, G.M. SHELXT—Integrated space-group and crystal-structure determination. *Acta Crystallogr. Sect. A Found. Crystallogr.* **2015**, *71*, 3–8. [CrossRef]