Controlled Growth of the Non-centrosymmetric Zn(3-ptz)2 and Zn(OH)(3-ptz) Metal-organic Frameworks

javier enriquez, Ignacio Chi-Duran, Carolina Manquian, Felipe Herrera, Ruben Fritz, Dinesh Pratap Singh

Submitted date: 15/01/2019 • Posted date: 16/01/2019
Licence: CC BY-NC-ND 4.0

Citation information: enriquez, javier; Chi-Duran, Ignacio; Manquian, Carolina; Herrera, Felipe; Fritz, Ruben; Singh, Dinesh Pratap (2019): Controlled Growth of the Non-centrosymmetric Zn(3-ptz)2 and Zn(OH)(3-ptz) Metal-organic Frameworks. ChemRxiv. Preprint.

Non-centrosymmetric single-crystal metal-organic frameworks (MOF) are promising candidates for phase-matched nonlinear optical communication, but typical hydrothermal synthesis produces small crystals with relatively low transmittance and poor phase matching. We study the effect of the metal-to-ligand molar ratio and reaction pH on the hydro-thermal synthesis of the non-centrosymmetric Zn(3-ptz)$_2$ and Zn(OH)(3-ptz) MOFs with in-situ ligand formation. In acidic environments, we find that decreasing the amount of ligand below the stoichiometric molar ratio 1:2 also produces highly transparent single-crystal octahedrons of Zn(3-ptz)$_2$. In alkaline environments, we obtain long rod-like Zn(OH)(3-ptz) crystals whose length exceeds previous reports by up to four orders of magnitude. Potential applications of these results in the development of MOF-based nonlinear optical devices are discussed.
Controlled growth of the non-centrosymmetric Zn(3-ptz)$_2$ and Zn(OH)(3-ptz) metal-organic frameworks

Javier Enríquez $^a$, Ignacio Chi-Duran $^b$, Carolina Manquian $^b$, Felipe Herrera $^{b,c}$ and Dinesh Pratap Singh $^{b,c}$

$^a$ Department of Metallurgical Engineering, Faculty of Engineering, University of Santiago, Av. Lib. Bernardo O’Higgins 3363, Estación Central, Santiago 10233, Chile

$^b$ Department of Physics, Universidad de Santiago de Chile, Avenida Ecuador 3493, Estación Central, 9170124 Santiago, Chile

$^c$ Millennium Institute for Research in Optics MIRO, Concepción, Chile

Non-centrosymmetric single-crystal metal-organic frameworks (MOF) are promising candidates for phase-matched nonlinear optical communication. However, the typical hydrothermal synthesis conditions produce small crystals with relatively low transmittance and poor phase matching. In the search for optimal crystal morphology we study the effect of the metal-to-ligand molar ratio and reaction pH on the hydro-thermal synthesis of the non-centrosymmetric Zn(3-ptz)$_2$ and Zn(OH)(3-ptz) MOFs with in-situ ligand formation. In acidic environments, we find that decreasing the amount of ligand below the stoichiometric molar ratio 1:2 also produces highly transparent single-crystal octahedrons of Zn(3-ptz)$_2$. In alkaline environments, we obtain long rod-like Zn(OH)(3-ptz) crystals whose length exceeds previous reports by up to four orders of magnitude. All reaction products are characterized by using p-XRD, FTIR and optical and scanning electron microscope. Additionally, we find an alternative synthesis route for the recently reported high-energy MOF Zn(3-ptz)N$_3$.

Potential applications of these results in the development of MOF-based nonlinear optical devices are discussed.

Introduction

Functional crystalline materials based on metal-organic frameworks (MOF) have been intensely studied over the past decade due to the diverse set of applications enabled by properties such as ultra-high porosity (1-6), record-high pore aperture size (5, 7), high thermal and chemical stability (8-13) and nonlinear optical activity (14-23). MOF materials have been successfully used for applications in gas storage and separation (24-27), fuel cells (28-31), chemical sensing (32-34), biomedical imaging (35-37) and drug delivery (38, 39). Several methods can be used to synthesize MOFs including microwave-assisted synthesis (40, 41), slow evaporation synthesis (42, 43), sonochemical synthesis (44, 45), mechanochemical synthesis (46, 47), electrochemical synthesis (48, 49) and hydro/solvo-thermal synthesis (50, 51). Different synthesis methods produce structures with characteristic size, homogeneity and morphology, which are directly related with the performance of the grown MOF crystals in applications. Therefore for each synthesis method, it is necessary to understand and control key synthesis parameters such as pH, temperature, pressure and metal-to-ligand molar ratio, in order to optimize the desired MOF structure for a target application.

The variation of the metal-to-ligand molar ratio in a MOF synthesis has been shown to affect the topology and dimensionality of the crystal structures. Wu et al. (52) reported the synthesis of [Zn(hfipbb)(H$_2$hfipbb)$_2$]$_n$, a 3D two fold parallel interpenetrating pillared network, and [Zn$_2$(hfipbb)$_2$(dps)(H$_2$O)]$_n$, a 3D bimodal-connected network with and without interpenetration, by varying the molar ratio M:L1:L2, where $M = Zn$, $L1 = H_2hfipbb$ [H$_2$hfipbb = 4,4’(hexafluoroisopropylidene) bis[benzoicacid]], and $L2 = dps$ [dps = 4,4’-dipyridylsulfide]. Similarly, Liu at al. (53) studied the effect of varying the metal-to-ligand molar ratio M:L with M=Co and L=btze [btze = 1, 2-bis(tetrazol- 1-yl)ethane], obtaining the 2D MOF [Co(btze)$_2$(SCN)$_2$]$_n$ as well as 1D linear chain [Co(btze)$_2$(SCN)$_2$]$_n$ for molar ratios 1:1 and 1:2, respectively. Yuan et al. (54) showed the activation of
different crystal growth patterns at a fixed molar ratio in M:L1:L2 mixtures, by varying the reaction pH. Higher pH values favored the formation of the 3D interpenetrating framework \([\text{Cd}_2(\text{CYP})_2]\text{n-2H}_2\text{O}\), whereas lower pH values facilitates the formation of the 3D MOF \([\text{Cd}_2(\text{CYP})_2(\text{ox})]_n\), without interpenetration.

Our work focuses on the synthesis of non-centrosymmetric MOFs with tetrazole-based ligands for which nonlinear optical activity is reported in powder form, for which phase-matching is not possible (55). Nonlinear optical MOF crystals could be used for applications in quantum cryptography based on entangled photon generation via spontaneous parametric down conversion (SPDC), a second-order nonlinear quantum optical process, provided that phase-matching conditions can be achieved. Tetrazole compounds are promising ligands for nonlinear optical MOFs formation due to their strong dipolar characteristics (56) and large optical response (57). From the synthetic point of view, tetrazole-based ligands are interesting because they possess a large number of coordination modes that can be selectively activated by varying the reaction pH, as recently demonstrated in Ref. (58) for the non-centrosymmetric MOF bis[5-(3-pyridyl)tetrazolato]zinc(II) \(\text{Zn(3-ptz)}_2\). This MOF crystal was first obtained by Wang et al. (59) using the Demko-Sharpless method for \textit{in-situ} formation of ligand 3-ptz starting from sodium azide \((\text{NaN}_3)\) and 3-cyanopyridine in the presence of a suitable Lewis acid, giving \(\text{Zn(3-ptz)}_2\) under hydro-thermal conditions for 24 hours at 105°C, using \(\text{ZnCl}_2\) as the Lewis acid catalyzer. We also produce the non-centrosymmetric MOF catena-\((\mu_3-\text{5-(3-pyridyl)}\text{tetrazol-N,N',N''})-(\mu_2-\text{hydroxo})-\text{zinc}\) \([\text{Zn(OH)(3-ptz)}_2]\), obtained previously under different conditions (60). The zinc \textit{tetr-aquo} coordination compound \(\text{Zn(H}_2\text{O})_4(3\text{-ptz})_2\) (59) is also obtained as a by-product. Besides, we report an alternative synthesis route for the non-porous 3D framework \([\text{Zn(3-ptz)}_2\text{N}_3]\), which exhibits energetic behavior due to the presence of structural azide groups in the unit cell (61). In Fig. 1 we plot the set of pH and metal-to-ligand molar ratios used in this and previous work.

In this work, we study the effect of varying the molar ratio of the metal salt \(\text{Zn(NO}_3)_2\) and the ligand precursor 3-cyanopyridine on the non-centrosymmetric MOF structures and other compounds obtained. Keeping constant the molar ratios at which pure MOFs crystals are obtained we also studied the variation of the mixing pH and corresponding structures are reported and analyzed. We summarize the reaction parameter space explored in this work in Figure 1. The use of zinc nitrate results in overall better crystals of \([\text{Zn(3-ptz)}_2]\) and \([\text{Zn(OH)(3-ptz)}]\) for a given pH and molar ratio, in comparison with the synthesis involving zinc chloride (59).

**Figure 1:** Reaction parameter space explored in this work, starting from zinc nitrate (squares). Previous results based on zinc chloride from Refs. (59) and (58) are also shown. The shaded region corresponds to experiments done without active pH control.

**Results and Discussion**
We first searched for an optimal metal-to-ligand molar ratio to obtain high-quality \([\text{Zn(3-ptz)}]_2\) crystals, by keeping the pH unaltered relative to previous work in Refs. (59) and (58). For the metal-to-ligand molar ratios 1:1 and 1:2, we varied the pH to search for improved crystal quality in terms of purity, yield and optical transparency.

Figure 2 shows the products obtained at different metal-to-ligand molar ratios such as 1:4, 1:2, 1:1 and 1:0.5, and further allowing the samples to cool down up to room temperature inside the furnace upon completion of the reaction time (24 h). In the stoichiometric ratio of 1:2 the pH was not controlled externally. The target compound is obtained for all molar ratio but the metal-to-ligand ratio of 1:0.5 favors the high purity and maximum growth of the crystals. The by-products obtained corresponding to each molar ratio are analyzed and summarized in Table 1. The pH reported are the pH measured immediately after mixing the reactants, without any additional steps of pH control. The corresponding optical images and powder x-ray diffraction patterns for each entry in Table 1 are shown in Figs. 2 and 3, respectively.

For the molar ratio 1:4, we obtain our target compound \([\text{Zn(3-ptz)}]_2\) as well as the zinc tetra aquo complex \([\text{Zn(H}_2\text{O})_4(3-\text{ptz})]_2\) (ZAC), which is obtained in relatively large quantities. The same products were obtained previously in Ref. (58) using half the amount of ligand. At the stoichiometric ratio 1:2, we obtain \([\text{Zn(3-ptz)}]_2\) along with very small quantities of non-reacting 3-cyanopyridine. This result should be compared with Ref. (58), which at same ratio (1:2) co-crystallization of ZAC and \([\text{Zn(3-ptz)}]_2\) is obtained without pH control. The difference in results in spite of having same reaction time, temperature and pressure, can only be attributed to the use of zinc nitrate (this work) salt instead of zinc chloride (58). In general, we obtain \([\text{Zn(3-ptz)}]_2\) crystals with improved size and transparency with zinc nitrate than with zinc chloride.

As we decrease the metal-to-ligand ratio below 1:2, we obtain increasing amounts of the recently reported energetic metal-organic framework \([\text{Zn(3-ptz)}]_4\) (mu-N)2-azido-[5-(3-pyridyl)tetrazolato]zinc(II), a non-porous MOF with 8 azide groups per unit cell (61). This energetic MOF does not exhibit explosive behavior at the conditions used for its synthesis, filtration, and its spectroscopic characterization. For the molar ratio 1:1, we obtain \([\text{Zn(3-ptz)}]_3\) along with our target compound, while decreasing the amount of ligand to the molar ratio 1:0.5 gives only \([\text{Zn(3-ptz)}]_3\) in high yield and high purity, which represents an alternative synthesis route in comparison with Ref.(61).

| Molar ratio | Mixing pH | Product | By-product |
|-------------|-----------|---------|------------|
| 1:4         | 6.00      | \([\text{Zn(3-ptz)}]_2\) | \([\text{Zn(H}_2\text{O})_4(3-\text{ptz})]_2\) |
| 1:2         | 5.81      | \([\text{Zn(3-ptz)}]_2\) | 3-Cyanopyridine |
| 1:1         | 5.49      | \([\text{Zn(3-ptz)}]_2\) | \([\text{Zn(3-ptz)}]_3\) |
| 1:0.5       | 5.20      | \([\text{Zn(3-ptz)}]_3\) | --------------- |
The powder XRD patterns in Figure 3 show that our target MOF Zn(3-ptz)$_2$ is present for metal-to-ligand molar ratios 1:4, 1:2 and 1:1. As expected, panel 3(b) shows that the stoichiometric ratio 1:2 gives a Zn(3-ptz)$_2$ crystal phase with higher purity. Residual peaks correspond to unreacted 3-cyanopyridine. Increasing the relative abundance of the ligand relative to the stoichiometric ratio, results in the formation of the aquo complex Zn(H$_2$O)$_4$(3-ptz)$_2$ along with Zn(3-ptz)$_2$. On the other hand, decreasing the relative abundance of the ligand relative to the stoichiometric ratio, enhances the growth of Zn(3-ptz)N$_3$. For molar ratio 1:1, Zn(3-ptz)N$_3$ is minority product. For molar ratio 1:0.5, the compound Zn(3-ptz)N$_3$ (stoichiometric ratio 1:1) is the main reaction product. For such a high molar ratio, there is no sufficient availability of 3-ptz ligands to form our target MOF.
Figure 3: Powder XRD patterns for the products listed in Table 1.

Figures 4 shows the SEM images for the samples listed in Table 1. Figure 4b clearly shows the octahedron morphology of the $\text{Zn}(3\text{-ptz})_2$ crystals formed. Crystal sizes obtained for $\text{Zn}(3\text{-ptz})_2$ in all experiments vary in the range 100-300 µm, which are typical sizes for reactions without pH control, all other reaction parameters the same as in Refs. (58, 59). For the stoichiometric metal-to-ligand ratio, the size of $\text{Zn}(3\text{-ptz})_2$ crystals is in general larger than those obtained at other molar ratios. This can be explained by the absence of competing nucleation events leading to the growth of by-product crystals, which also consume 3-ptz ligands. Figure 4a shows that the smaller by-product crystals $\text{Zn}$(H$_2$O)$_4$(3-ptz)$_2$ grow on the surface of $\text{Zn}(3\text{-ptz})_2$ crystals. The SEM images of the energetic MOF $\text{Zn}(3\text{-ptz})N_3$ crystals are shown in Fig. 4c,d. The crystal size varies in the range 300 – 700 µm.
We also measure the FTIR spectra of the products listed in Table 1. We observe the characteristic peaks for tetrazole near 1500 cm\(^{-1}\) in all samples. The broad OH band peaked at 3250 cm\(^{-1}\) is also present for the molar ratio 1:4, associated with the \textit{aquo} complex \(\text{Zn(H}_2\text{O)}_4(3\text{-ptz})_2\). Fig. 5a shows, that at the stoichiometric ratio 1:2, the FTIR spectrum exhibits a weak peak at 2073 cm\(^{-1}\), which can be assigned to the -CN bond of unreacted 3-cyanopyridine. For the molar ratio 1:1, a strong and narrow peak is observed at 2070 cm\(^{-1}\), which can be assigned to the azido group (-N\(_3\)) that forms the energetic MOF \(\text{Zn(3-ptz)N}_3\). The strong azido IR peak (-N\(_3\)) is also present for repetitions for the synthesis at molar ratio 1:0.5, for which \(\text{Zn(3-ptz)N}_3\) is the main product.
Controlling the reaction pH at fixed molar ratio

In addition to variation of molar ratio, we explore the effect of changing the pH of the solution at the stage of mixing the reactants whereas during the reaction in the furnace the pH is unmonitored. We vary the pH as described in Ref. (58) for two sets of experiments. One set for the molar ratio 1:2, which is the stoichiometric ratio of Zn(3-ptz)$_2$, and another set for the molar ratio 1:1, which is the stoichiometric ratio of Zn(3-ptz)N$_3$. The main products obtained in each set of experiments are summarized in Tables 2 and 3.

For the molar ratio 1:2 (Table 2), our results are qualitatively in agreement with those in Ref. (58). In general, increasing the mixing pH above the uncontrolled pH level (5.81) favors the formation of the two-dimensional MOF Zn(OH)(3-ptz) (58, 60), as the ions Zn(OH)$^+$ and Zn(OH)$_2^-$ become the most abundant species (>99%) in the pH range 6 – 11, at 75ºC (62). Near pH 13 we obtain an almost exclusive formation of zinc oxide (ZnO), in agreement with Ref. (58). Powder XRD and FTIR spectra confirm these results as shown in the Supplementary Material (SM).

We obtain roughly the same total crystal yield and reaction products in the case of uncontrolled pH (5.81) and at pH 4.67, controlled with nitric acid. The powder XRD spectra for both samples are indistinguishable (see SM), both confirming the presence of Zn(3-ptz)$_2$ and 3-cyanopyridine. The optical images in Fig. 6 show that at pH 4.67, the Zn(3-ptz)$_2$ octahedrons co-exist with large 3-cyanopyridine molecular crystals, whose observed habit is consistent with simulations. The more intense -CN peak in the IR spectrum shown in Fig. 7a, confirms the greater abundance of unreacted 3-cyanopyridine at lower pH in comparison with pH 5.81. Unreacted 3-cyanopyridine can result from the protonation of azide ions (N$_3^-$) at low pH. As the azide ion captures a proton, its availability to participate in the cycloaddition reaction that forms 3-pto ligands (63) is significantly reduced.

| pH    | Product   | Sub-product |
|-------|-----------|-------------|
| 4.67  | Zn(3-ptz)$_2$ | 3-Cyanopyridine |
| *5.81 | Zn(3-ptz)$_2$ | 3-Cyanopyridine |
| 7.66  | Zn(OH)(3-ptz) | ZnO |
| 10.01 | Zn(OH)(3-ptz) | ZnO |
| 13.08 | ZnO | |

Table 2: Main products obtained at different pH for the metal-to-ligand molar ratio 1:2. The pH labeled with an asterisk coincides with Table 1.

| pH    | Product   | Sub-product |
|-------|-----------|-------------|
| 3.90  | Zn(3-ptz)$_2$ | 3-Cyanopyridine |
| *5.49 | Zn(3-ptz)$_2$ | Zn(3-ptz)N$_3$ |
| 7.96  | Zn(OH)(3-ptz) | ZnO |
| 11.01 | Zn(OH)(3-ptz) | ZnO |
| 13.84 | ZnO | |

Table 3: Main products obtained at different pH for the metal-to-ligand molar ratio 1:1. The pH labeled with an asterisk coincides with Table 1.
Figure 6: Optical images for samples in Table 2 at pH 4.67 (panel a) and pH 5.81 (panel b), for metal-to-ligand molar ratio 1:2. The simulated crystal habits of 3-cyanopyridine (panel c) and Zn(3-ptz)$_2$ (panel d) are also shown.
Figure 7: FTIR spectra selected samples from Table 2, for metal-to-ligand molar ratio 1:2.

Figure 8 shows the SEM images of the samples in Table 2. Panels a-d show the \textbf{Zn(3-ptz)$_2$} MOF octahedrons obtained at the low pH, whose size vary in the range 100 – 300 µm. For alkaline environments (pH 7.77 and 10.01), we obtain the large rod-like structures characteristic of MOF crystal \textbf{Zn(OH)(3-ptz)}, which has a 2D coordination framework (58, 60). At pH 10.01, we obtain large micro-rods with lengths in the range 300 µm – 1.8 mm, which is $10^4$ times higher than previously reported (58, 60), for the same reaction times and temperatures. The rod widths vary in the range 2 – 30 µm, which is up to ten times higher as previous reports. We attribute this improvement in size to the use of zinc nitrate instead of zinc chloride (58, 60).
In a second set of experiments, we fixed to 1:1 the metal-to-ligand molar ratio, which is the stoichiometric ratio for the energetic MOF Zn(3-ptz)N$_3$ (61), varying the mixing pH as specified in Table 3. Figure 9 shows the optical images of the products obtained at pH 3.90 and 5.49. The corresponding powder XRD patterns are given in Fig. 10a,b. Despite obtaining similar total crystal yields, and having generated our target MOF Zn(3-ptz)$_2$ for the two acidic conditions explored, the overall results are qualitatively different. While Fig. 10b shows that without active pH control (pH 5.49), a significant amount of Zn(3-ptz)N$_3$ is formed in a mixed phase with Zn(3-ptz)$_2$, at pH 3.90 there are no traces of the energetic compound. We understand this in terms of a lower availability of azide ions N$_3^-$ to form coordination bonds with zinc at lower pH. At the mixing
temperature (25°C), the relative abundance of azide ions in solution is less than 13% (pKa=4.72 (64)). On the other hand, for pH 5.49, the relative abundance of azide ions is about 85%. Figure 10c shows that at pH 7.96, we obtain predominantly Zn(OH)(3-ptz) and ZnO. Additional XRD data confirms (not shown) that as the pH is increased beyond 8.0, the growth of ZnO is favored over Zn(OH)(3-ptz).

Figure 9: Optical images for samples in Table 3 at pH 3.90 (panel a) and pH 5.49 (panel b), for metal-to-ligand molar ratio 1:1.

Figure 10: Powder XRD patterns of the products listed in Table 3, for pH 3.90 (panel a), pH 5.49 (panel b), and pH 7.96 (panel c).
CONCLUSIONS

We explored a set of hydrothermal synthesis parameters to optimize the production of the transparent non-centrosymmetric MOFs [Zn(3-ptz)₃] and [Zn(OH)(3-ptz)], which have been proposed for applications in nonlinear optical signal processing with phase matching. By varying the metal-to-ligand molar ratio and the mixing pH, we find that high-quality [Zn(3-ptz)₃] can be obtained in large quantities at the molar ratios 1:2 and 1:1. For the molar ratio 1:2 and pH around 4.2 the [Zn(3-ptz)₃] crystals with improved transparency and purity is obtained. In alkaline environments (pH 7 – 10), we obtain large rod-like [Zn(OH)(3-ptz)] crystals with lengths reaching up to the millimeter regime. This is a four-order of magnitude improvement over previous reports. All samples were obtained using nitrate (NO₃⁻) as the zinc counter ion, which is found to give higher quality crystals in comparison with previously used zinc chloride salts. As an additional result, we found a simple alternative synthesis route for [Zn(3-ptz)N₃], a high-energy MOF that has been recently reported (61).

The results obtained are promising for the development of MOF-based nonlinear optical devices. The high transparency and increasing size of the [Zn(3-ptz)₃] crystals obtained at lower mixing pH show the potential for further optimization of the reaction acidity. Reaching single crystal sizes in the millimeter regime would enable optical characterization such as Mueller polarimetry as well second-harmonic generation (SHG) with phased-matching. Moreover, the record lengths obtained for the [Zn(OH)(3-ptz)] crystals would facilitate the simple alignment of the rod-like structures on a substrate using mechanical stress. Such aligned quasi-1D crystals can be used as nonlinear waveguides for efficient generation of SHG signals using standard microscopy techniques. Nonlinear optical MOF waveguides would allow the development of alternative materials for scalable integrated quantum photonics (65).

Methods

The Zn-to-(3-ptz) molar ratio (metal-to-ligand) was varied by using 1 mmol, 2 mmol, 4 mmol and 8 mmol of Zn(NO₃)₂·6H₂O, keeping the amount of 3-Cyanopyridine and NaN₃ fixed to 4 mmol and 6 mmol, respectively. The corresponding molar ratios are 1:4, 1:2, 1:1 and 1:0.5. All reagents were mixed in a bottle with a screw cap, 6 ml of distilled water were added at room temperature. After measuring the pH of the solution, this is put to the oven for 24 hours at 105 °C. The samples were left for another 24 hours inside the oven for cooling to room temperature. After cooling, the obtained samples were washed with ethanol and left for another 24 hours to dessicate in vacuum. For the set of experiments at fixed molar ratios 1:2 and 1:1, the pH is fixed by using nitric acid at 70% (Sigma Aldrich) and KOH 18,8 [M] after mixing the reactants with distilled water at room temperature. The reaction procedure follows as described above. For the set of experiments with molar ratio 1:1, the samples are quickly filtered in hot with a kitasato and a vacuum pump, then washed with ethanol and vacuum-stored in the desiccator for 24 hours. X-ray diffraction analysis was done with a Shimazdu XRD 6000 diffractometer using Cu Kα (l = 1.5418 Å) radiation. Microstructural characterization of the synthesized materials was done by scanning electron microscope Zeiss EVO MA10. pH was measured with pH meter 2700 OAKTON. FTIR measurements were taken with a JASCO FTIR-4600 Spectrophotometer equipped with an ATR PRO ONE.

Acknowledgments

We thank Gustavo Cañas for helpful suggestions. J.E. and D.P.S. are supported by Proyecto Basal USA 1799 VRIDEI and Fondecyt Regular 1151527. F.H. is supported by CONICYT through the Proyecto REDES ETAPA INICIAL, Convocatoria 2017 No. REDI 170423, and FONDECYT Regular No. 1181743. F. H. and D.P.S also thank support by Iniciativa Científica Milenio (ICM) through the Millennium Institute for Research in Optics.
References

1. Yaghi OM, Li H. Hydrothermal Synthesis of a Metal-Organic Framework Containing Large Rectangular Channels. Journal of the American Chemical Society. 1995;117(41):10401-2.
2. Li H, Eddaoudi M, O’Keeffe M, Yaghi OM. Design and synthesis of an exceptionally stable and highly porous metal-organic framework. Nature. 1999;402(6759):276-9.
3. Furukawa H, Yaghi OM. Storage of Hydrogen, Methane, and Carbon Dioxide in Highly Porous Covalent Organic Frameworks for Clean Energy Applications. Journal of the American Chemical Society. 2009;131(25):8875-83.
4. Farha OK, Eryazici I, Jeong NC, Hauser BG, Wilmer CE, Sarjeant AA, et al. Metal–Organic Framework Materials with Ultrahigh Surface Areas: Is the Sky the Limit? Journal of the American Chemical Society. 2012;134(36):15016-21.
5. Deng H, Grunder S, Cordova KE, Valente C, Furukawa H, Hmadeh M, et al. Large-Pore Apertures in a Series of Metal-Organic Frameworks. Science. 2012;336(6084):1018-23.
6. Farha OK, Özgür Yazaydın A, Eryazici I, Malliakas CD, Hauser BG, Kanatzidis MG, et al. De novo synthesis of a metal–organic framework material featuring ultrahigh surface area and gas storage capacities. Nat Chem. 2010;2(11):944-8.
7. Rosi NL, Kim J, Eddaoudi M, Chen B, O’Keeffe M, Yaghi OM. Rod Packings and Metal–Organic Frameworks Constructed from Rod-Shaped Secondary Building Units. Journal of the American Chemical Society. 2005;127(5):1504-18.
8. Eddaoudi M, Kim J, Rosi N, Vodak D, Wachter J, O’Keeffe M, et al. Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Application in Methane Storage. Science. 2002;295(5554):469-72.
9. Park KS, Ni Z, Côté AP, Choi JY, Huang R, Uribe-Romo FJ, et al. Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. Proceedings of the National Academy of Sciences. 2006;103(27):10186-91.
10. Cavka JH, Jakobsen S, Olsbye U, Guillou N, Lamberti C, Bordiga S, et al. A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability. Journal of the American Chemical Society. 2008;130(42):13850-1.
11. Kandiah M, Nilsen MH, Usseglio S, Jakobsen S, Olsbye U, Tilset M, et al. Synthesis and Stability of Tagged UiO-66 Zr-MOFs. Chemistry of Materials. 2010;22(24):6632-40.
12. Morris W, Volosskii B, Demir S, Gándara F, McGrier PL, Furukawa H, et al. Synthesis, Structure, and Metalation of Two New Highly Porous Zirconium Metal–Organic Frameworks. Inorganic Chemistry. 2012;51(12):6443-5.
13. Colombo V, Galli S, Choi HJ, Han GD, Maspero A, Palmisano G, et al. High thermal and chemical stability in pyrazolate-bridged metal-organic frameworks with exposed metal sites. Chemical Science. 2011;2(7):1311-9.
14. Lin W, Ma L, Evans OR. NLO-active zinc(ii) and cadmium(ii) coordination networks with 8-fold diamondoid structures. Chemical Communications. 2000(22):2263-4.
15. Du F, Zhang H, Tian C, Du S. Synthesis and Structure of Two Acentric Heterometallic Inorganic–Organic Hybrid Frameworks with Both Nonlinear Optical and Ferroelectric Properties. Crystal Growth & Design. 2013;13(4):1736-42.
16. Ye Q, Li Y-H, Song Y-M, Huang X-F, Xiong R-G, Xue Z. A Second-Order Nonlinear Optical Material Prepared through In Situ Hydrothermal Ligand Synthesis. Inorganic Chemistry. 2005;44(10):3618-25.
17. Ma S, Fillinger JA, Ambrogio MW, Zuo J-L, Zhou H-C. Synthesis and characterizations of a magnesium metal–organic framework with a distorted (10,3)-a-netology. Inorganic Chemistry Communications. 2007;10(2):220-2.
18. Liu Y, Li G, Li X, Cui Y. Cation-Dependent Nonlinear Optical Behavior in an Octupolar 3D Anionic Metal–Organic Open Framework. Angewandte Chemie International Edition. 2007;46(33):6301-4.
19. Lin W, Evans OR, Xiong R-G, Wang Z. Supramolecular Engineering of Chiral and Acentric 2D Networks. Synthesis, Structure, and Second-Order Nonlinear Optical Properties of Bis(nicotinato)zinc and Bis[3-[2-(4-pyridyl)ethenyl]benzoato]cadmium. Journal of the American Chemical Society. 1998;120(50):13272-3.
20. Evans OR, Lin W. Rational Design of Nonlinear Optical Materials Based on 2D Coordination Networks. Chemistry of Materials. 2001;13(9):3009-17.
21. Zhang H, Wang X, Teo BK. Molecular Design and Crystal Engineering of a New Series of Inorganic Polymers Separated by Organic Spacers: Structures of [(18C6)K][Cd(SCN)3] and [(18C6)2Na2(H2O)2]1/2[Cd(SCN)3]. Journal of the American Chemical Society. 1996;118(47):11813-21.
22. Han L, Hong M, Wang R, Luo J, Lin Z, Yuan D. A novel nonlinear optically active tubular coordination network based on two distinct homo-chiral helices. Chemical Communications. 2003(20):2580-1.
23. Wang C, Zhang T, Lin W. Rational Synthesis of Noncentrosymmetric Metal–Organic Frameworks for Second-Order Nonlinear Optics. Chemical Reviews. 2012;112(2):1084-104.
24. Rosi NL, Eckert J, Eddaoudi M, Vodak DT, Kim J, O'Keefe M, et al. Hydrogen Storage in Microporous Metal-Organic Frameworks. Science. 2003;300(5622):1127-9.

25. Ferey G, Latroche M, Serre C, Millange F, Loiseau T, Percheron-Guegan A. Hydrogen adsorption in the nanoporous metal-benzenedicarboxylate M(OH)[O2C-C6H4-CO2] (M = Al3+, Cr3+), MIL-53. Chemical Communications. 2003(24):2976-7.

26. Loiseau T, Serre C, Huguenard C, Fink G, Taulelle F, Henry M, et al. A Rationale for the Large Breathing of the Porous Aluminum Terephthalate (MIL-53) Upon Hydration. Chemistry – A European Journal. 2004;10(6):1373-82.

27. Chen B, Ockwig NW, Millward AR, Contreras DS, Yaghi OM. High H2 Adsorption in a Microporous Metal–Organic Framework with Open Metal Sites. Angewandte Chemie International Edition. 2005;44(30):4745-9.

28. Nagao Y, Ikeda R, Kanda S, Kubozono Y, Kitagawa H. Complex-Plane Impedance Study on a Hydrogen-Doped Copper Coordination Polymer: N,N'-bis-(2-hydroxyethyl)dithiooxamidato-copper(II). Molecular Crystals and Liquid Crystals. 2002;379(1):89-94.

29. Shigematsu A, Yamada T, Kitagawa H. Wide Control of Proton Conductivity in Porous Coordination Polymers. Journal of the American Chemical Society. 2011;133(7):2034-6.

30. Taylor JM, Dawson KW, Shimizu GKH. A Water-Stable Metal–Organic Framework with Highly Acidic Pores for Proton-Conducting Applications. Journal of the American Chemical Society. 2013;135(4):1193-6.

31. Yamada T, Sadakiyo M, Kitagawa H. High Proton Conductivity of One-Dimensional Ferrous Oxalate Dihydrate. Journal of the American Chemical Society. 2009;131(9):3144-5.

32. Xie Z, Ma L, deKrafft KE, Jin A, Lin W. Porous Phosphorescent Coordination Polymers for Oxygen Sensing. Journal of the American Chemical Society. 2010;132(3):922-3.

33. Chen B, Wang L, Xiao Y, Fronczek FR, Xue M, Cui Y, et al. A Luminescent Metal–Organic Framework with Lewis Basic Pyridyl Sites for the Sensing of Metal Ions. Angewandte Chemie International Edition. 2009;48(3):500-3.

34. Lan A, Li K, Wu H, Olson DH, Emge TJ, Ki W, et al. A Luminescent Microporous Metal–Organic Framework for the Fast and Reversible Detection of High Explosives. Angewandte Chemie International Edition. 2009;48(13):2334-8.

35. Della Rocca J, Lin W. Nanoscale Metal–Organic Frameworks: Magnetic Resonance Imaging Contrast Agents and Beyond. European Journal of Inorganic Chemistry. 2010;2010(24):3725-34.

36. Liu D, Huxford RC, Lin W. Phosphorescent Nanoscale Coordination Polymers as Contrast Agents for Optical Imaging. Angewandte Chemie International Edition. 2011;50(16):3696-700.

37. Lin W, Rieter WJ, Taylor KML. Modular Synthesis of Functional Nanoscale Coordination Polymers. Angewandte Chemie International Edition. 2009;48(4):650-8.

38. Rieter WJ, Pott KM, Taylor KML, Lin W. Nanoscale Coordination Polymers for Platinum-Based Anticancer Drug Delivery. Journal of the American Chemical Society. 2008;130(35):11584-5.

39. Huxford RC, Della Rocca J, Lin W. Metal–organic frameworks as potential drug carriers. Current Opinion in Chemical Biology. 2010;14(2):262-8.

40. Bag PP, Wang X-S, Cao R. Microwave-assisted large scale synthesis of lanthanide metal-organic frameworks (Ln-MOFs), having a preferred conformation and photoluminescence properties. Dalton Transactions. 2015;44(26):11954-62.

41. Klinowski J, Almeida Paz FA, Silva P, Rocha J. Microwave-Assisted Synthesis of Metal-Organic Frameworks. Dalton Transactions. 2011;40(2):321-30.

42. Zou R-Q, Jiang L, Senoh H, Takeichi N, Xu Q. Rational assembly of a 3D metal-organic framework for gas adsorption with predefined cubic building blocks and 1D open channels. Chemical Communications. 2005(28):3526-8.

43. Li P, He Y, Guang J, Weng L, Zhao JC-G, Xiang S, et al. A Homochiral Microporous Hydrogen-Bonded Organic Framework for Highly Enantioselective Separation of Secondary Alcohols. Journal of the American Chemical Society. 2014;136(2):547-9.

44. Karizi FZ, Safarifard V, Khani SK, Morsali A. Ultrasound-assisted synthesis of nano-structured 3D zinc(II) metal–organic polymer: Precursor for the fabrication of ZnO nano-structure. Ultrasonics Sonochemistry. 2015;23:238-45.

45. Mehrani A, Morsali A, Hanifehpour Y, Joo SW. Sonochemical temperature controlled synthesis of pellet-, laminate- and rice grain-like morphologies of a Cu(II) porous metal–organic framework nano-structures. Ultrasonics Sonochemistry. 2014;21(4):1430-4.

46. Pilloni M, Padella F, Ennas G, Lai S, Belluscì M, Rombi E, et al. Liquid-assisted mecanochemical synthesis of an iron carboxylate Metal Organic Framework and its evaluation in diesel fuel desulfurization. Microporous and Mesoporous Materials. 2015;213:14-21.
47. Yan D, Gao R, Wei M, Li S, Lu J, Evans DG, et al. Mechanochemical synthesis of a fluorenone-based metal organic framework with polarized fluorescence: an experimental and computational study. Journal of Materials Chemistry C. 2013;1(5):997-1004.

48. Campagnol N, Souza ER, De Vos DE, Binnemans K, Fransaer J. Luminescent terbium-containing metal-organic framework films: new approaches for the electrochemical synthesis and application as detectors for explosives. Chemical Communications. 2014;50(83):12545-7.

49. Martinez Joaristi A, Juan-Alcañiz J, Serra-Crespo P, Kapteijn F, Gascon J. Electrochemical Synthesis of Some Archetypical Zn2+, Cu2+, and Al3+ Metal Organic Frameworks. Crystal Growth & Design. 2012;12(7):3489-98.

50. Bo Q-B, Pang J-J, Wang H-Y, Fan C-H, Zhang Z-W. Hydrothermal synthesis, characterization and photoluminescence properties of the microporous metal organic frameworks with 1,3-propanediaminetetraacetate ligand and its auxiliary ligand. Inorganica Chimica Acta. 2015;428:170-5.

51. Saha D, Maity T, Koner S. Alkaline earth metal-based metal-organic framework: hydrothermal synthesis, X-ray structure and heterogeneously catalyzed Claissen-Schmidt reaction. Dalton Transactions. 2014;43(34):13006-17.

52. Wu Y-P, Li D-S, Fu F, Dong W-W, Zhao J, Zou K, et al. Stoichiometry of N-Donor Ligand Mediated Assembly in the Znll-Hfi pb b System: From a 2-Fold Interpenetrating Pillared-Network to Unique (3,4)-Connected Isomeric Nets. Crystal Growth & Design. 2011;11(9):3850-7.

53. Liu P-P, Cheng A-L, Yue Q, Liu N, Sun W-W, Gao E-Q. Cobalt(II) Coordination Networks Dependent upon the Spacer Length of Flexible Bis(tetrazole) Ligands. Crystal Growth & Design. 2008;8(5):1668-74.

54. Yuan F, Xie J, Hu H-M, Yuan C-M, Xu B, Yang M-L, et al. Effect of pH/metal on the structure of metal-organic frameworks based on novel bifunctionalized ligand 4[prime or minute]-carboxy-4,2[prime or minute]-6[prime or minute]-4[prime or minute]-terpyridine. CrystEngComm. 2013;15(7):1460-7.

55. W Boyd R. Nonlinear Optics Second Edition2003.

56. Liu D-S, Sui Y, Chen W-T, Feng P. Two New Nonlinear Optical and Ferroelectric Zn(II) Compounds Based on Nicotinic Acid and Tetrazole Derivative Ligands. Crystal Growth & Design. 2015;15(8):4020-5.

57. Zheng Y, Wang S-H, Wu S-F, Zheng F-K, Wu AQ. Tunable photoluminescence of a dual-emissive zinc(II) coordination polymer with an in-situ generated tetrazole derivative and benzenetetracarboxyli. Inorganic Chemistry Communications. 2015;53:20-2.

58. Chi-Durán I, Enríquez J, Manquian C, Wrighton-Araneda K, Cañon-Mancisidor W, Venegas-Yazigi D, et al. pH-Controlled Assembly of 3D and 2D Zinc-Based Metal-Organic Frameworks with Tetrazole Ligands. ACS Omega. 2018;3(1):801-7.

59. Wang L-Z, Qu Z-R, Zhao H, Wang X-S, Xiong R-G, Xue Z-L. Isolation and Crystallographic Characterization of a Solid Precipitate/Intermediate in the Preparation of 5-Substituted 1H-Tetrazoles from Nitrile in Water. Inorganic Chemistry. 2003;42(13):3969-71.

60. Xiong R-G, Xue X, Zhao H, You X-Z, Abrahams BF, Xue Z. Novel, Acentric Metal–Organic Coordination Polymers from Hydrothermal Reactions Involving In Situ Ligand Synthesis. Angewandte Chemie International Edition. 2002;41(20):3800-3.

61. Ignacio C-D, Carolina M, Daniel S, javier e, Felipe H, Dinesh Pratap S. Azide-Based High-Energy Metal-Organic Framework with Enhanced Thermal Stability2018.

62. Reichle RA, McCurdy KG, Hepler LG. Zinc Hydroxide: Solubility Product and Hydroxy-complex Stability Constants from 12.5–75 °C. Canadian Journal of Chemistry. 1975;53(24):3841-5.

63. Demko ZP, Sharpless KB. Preparation of 5-Substituted 1H-Tetrazoles from Nitriles in Water. The Journal of Organic Chemistry. 2001;66(24):7945-50.

64. Patnaik P. Handbook of inorganic chemicals: McGraw-Hill New York; 2003.

65. Moebius MG, Herrera F, Griesse-Nascimento S, Reshef O, Evans CC, Guerreschi GG, et al. Efficient photon triplet generation in integrated nanophotonic waveguides. Opt Express. 2016;24(9):9932-54.
