Controlled Growth of the Noncentrosymmetric Zn(3-ptz)2 and Zn(OH)(3-ptz) Metal−Organic Frameworks

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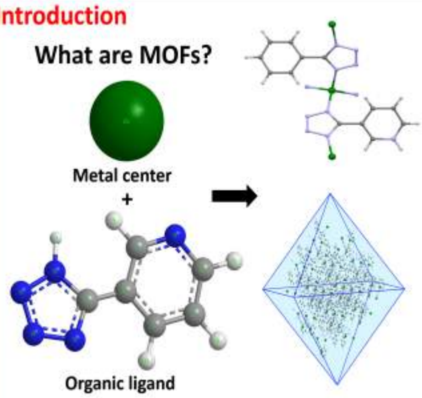
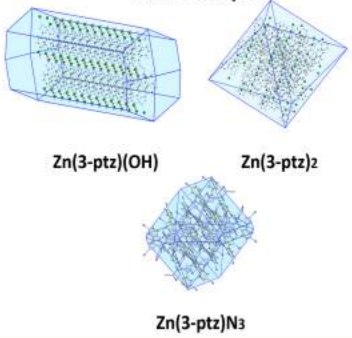
Introduction

What are MOFs?



Why change molar ratio and pH?



MOFs for second order nonlinear optics

General structure

- **Noncentrosymmetric structure.**

Metal

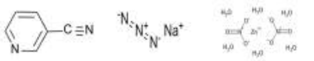
- **Avoid unwanted d-d transitions in the visible region, d^{10} metal ions .**

Ligand

- **Change in the value of the dipole when going from the base state to the exited state.**
- **ligand-metal is able to form a noncentrosymmetric.**

Methodology

3-cyanopyridine (4mmol) + NaN_3 (6mmol) + $Zn(NO_3)_2{\cdot}6H_2O$ (changeable mmol)



Mixed in a bottle with a screw cap and 6 ml of distilled water was added. To modify pH was using HNO_3 and KOH.

The samples were kept in an oven for 24 h at 105 °C and cooled to room temperature.

Variation of molar ratio between $Zn(NO_3)_2$ and 3-cyanopyridine

$Zn(NO_3)_2$ mmol	Molar ratio
8	1:0.5
4	1:1
2	1:2
1	1:4

Variation of pH at 1:2 molar ratio

pH
4.67
5.81
7.66
10.01
13.08

Variation of pH at 1:1 molar ratio

pH
3.90
5.49
7.96
11.01
13.84

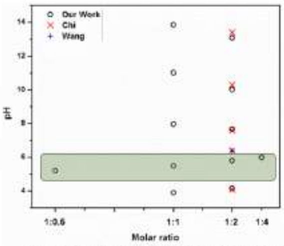


Figure 1. Reaction parameter space explored in this work starting from zinc nitrate.

Result and discussion

Table 1. Main Product and Byproduct Obtained at Room Temperature for Different Metal-to-Ligand Molar Ratios without pH Control

molar ratio	mixing pH	product	byproduct
1:4	6.00	$Zn(3\text{-}ptz)_2$	$Zn(H_2O)_4(3\text{-}ptz)_2$
1:2	5.81	$Zn(3\text{-}ptz)_2$	3-cyanopyridine
1:1	5.49	$Zn(3\text{-}ptz)_2$	$Zn(3\text{-}ptz)N_3$
1:0.5	5.20	$Zn(3\text{-}ptz)N_3$	

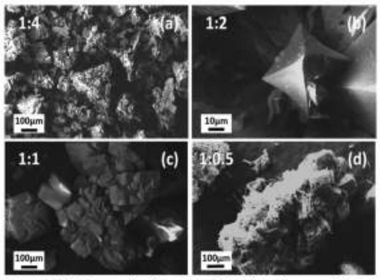


Figure 2. SEM images for the as-synthesized products at different metal-to-ligand molar ratios 1:4 (a), 1:2 (b), 1:1 (c), and 1:0.5 (d).

Table 2. Products As Obtained at Different pH for the Metal-to-Ligand Molar Ratio 1:2[a]

pH	product	subproduct
4.67	$Zn(3\text{-}ptz)_2$	3-cyanopyridine
*5.81	$Zn(3\text{-}ptz)_2$	3-cyanopyridine
7.66	$Zn(OH)(3\text{-}ptz)$	ZnO
10.01	$Zn(OH)(3\text{-}ptz)$	ZnO
13.08	ZnO	

[a] The pH labeled with an asterisk coincides with Table 1.

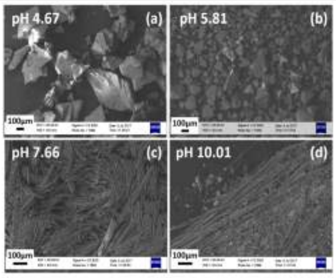


Figure 3. (a−d) SEM images of the samples at different pH for the constant metal-to-ligand molar ratio of 1:2.

Table 3. Products As Obtained at Different pH for the Metal-to-Ligand Molar Ratio 1:1[a]

pH	product	subproduct
3.90	$Zn(3\text{-}ptz)_2$	3-cyanopyridine
*5.49	$Zn(3\text{-}ptz)_2$	$Zn(3\text{-}ptz)N_3$
7.96	$Zn(OH)(3\text{-}ptz)$	ZnO
11.01	$Zn(OH)(3\text{-}ptz)$	ZnO
13.84	ZnO	

[a] The pH labeled with an asterisk coincides with Table 1.

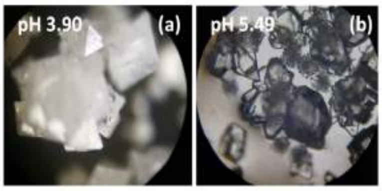


Figure 4. Optical images for samples in Table 3 at pH = 3.90 (a) and pH 5.49 (b) for the metal-to-ligand molar ratio 1:1.

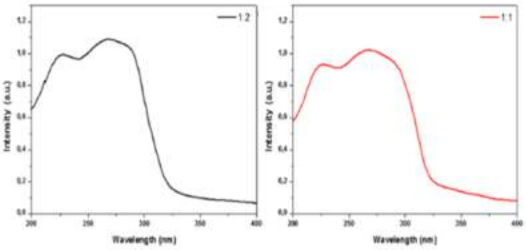


Figure 5: UV−visible absorption spectra of both samples 1:2 and 1:1

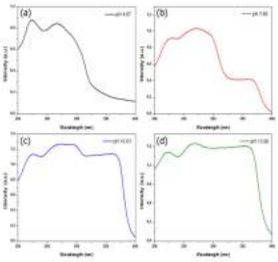


Figure 6. UV−vis solid spectra of the samples at different pH of 4.67 (a), 7.66 (b), 10.01 (c), and 13.08 (d) for the metal-to-ligand molar ratio 1:2.

Conclusions

1. We explored a set of hydrothermal synthesis parameters to optimize the growth of the transparent noncentrosymmetric. MOFs $Zn(3\text{-}ptz)_2$ and Zn(OH)(3-ptz), which have been proposed for applications in nonlinear optical signal processing with phase matching.
2. By varying the metal-to-ligand molar ratio and the mixing pH, we find that high-quality $Zn(3\text{-}ptz)_2$ 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 $Zn(3\text{-}ptz)_2$ crystals with improved transparency and purity are obtained.
3. In alkaline environments (pH 7−10), we obtain large rodlike Zn(OH)(3-ptz) crystals with lengths approaching to the millimeter regime. This is a 4 order of magnitude improvement over previous reports.
4. The results obtained are promising for the development of MOF-based nonlinear optical devices. The high transparency and increasing size of the $Zn(3\text{-}ptz)_2$ crystals obtained at lower mixing pH show the potential for further optimization of the reaction acidity. Reaching to single-crystal sizes in the millimeter regime would enable optical characterization such as Mueller polarimetry as well as SHG with phase matching.

Acknowledgments

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