



Aalborg Universitet

AALBORG UNIVERSITY  
DENMARK

## Effect of Zn/Co node ratio on the glass transition in the high-density amorphous ZIF-4

Du, Z.J. ; Qiao, A.; Zhou, H.M.; Tao, H.Z.; Yue, Yuanzheng

*Publication date:*  
2023

*Document Version*  
Publisher's PDF, also known as Version of record

[Link to publication from Aalborg University](#)

*Citation for published version (APA):*

Du, Z. J., Qiao, A., Zhou, H. M., Tao, H. Z., & Yue, Y. (2023). *Effect of Zn/Co node ratio on the glass transition in the high-density amorphous ZIF-4*. Abstract from International Commission on Glass Annual Meeting 2023, Hangzhou, China.

### General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal -

### Take down policy

If you believe that this document breaches copyright please contact us at [vbn@aub.aau.dk](mailto:vbn@aub.aau.dk) providing details, and we will remove access to the work immediately and investigate your claim.

# Effect of Zn/Co node ratio on the glass transition in the high-density amorphous ZIF-4

Zijuan Du<sup>1\*</sup>, Ang Qiao<sup>1</sup>, Hemin Zhou<sup>1</sup>, Haizheng Tao<sup>1</sup>, Yuanzheng Yue<sup>2</sup>

<sup>1</sup> State Key Laboratory of Silicate Materials for Architectures (Wuhan University of Technology),  
Wuhan 430070, China.

<sup>2</sup> Department of Chemistry and Bioscience, Aalborg University, DK-9220 Aalborg, Denmark.

\*Email: zijuan.du@ucl.ac.uk

**Abstract:** Zeolitic imidazolate frameworks (ZIFs) are an important subset of Metal-organic framework (MOF) glasses, which have been utilized for various applications. Upon heating, ZIF-4 crystals experience a polyamorphic transition, i.e., the transformation of a super-strong (i.e., very low liquid fragility in Angell's sense) low-density liquid into a relatively "fragile" high-density liquid.[1] Upon cooling, the latter transforms into the high-density amorphous phase (HDA). Understanding the connection between the glass transition temperature ( $T_g$ ) and structural factors is crucial for processing the ZIF liquid phase with desired properties. By reheating the quenched HDA, the glass-to-liquid transition occurs. Despite notable progress in studying ZIF glasses, the nature of the HDA of ZIFs remains to be revealed. Particularly, the influence of metal node substitution on  $T_g$  of the ZIF-4 HDA has not yet been investigated. Here, we report the preparation of bimetallic Zn/Co-ZIF-4 HDAs and their  $T_g$  values [2]. The temperature dependence of the isobaric heat capacity ( $C_p$ ) of ZIF-4 HDAs was measured to determine the  $T_g$ . The  $T_g$  non-linearly decreases with the molar ratio  $R$ , where  $R$  is  $\text{Co}/(\text{Co}+\text{Zn})$ , indicating the presence of a mixed-metal node effect [3]. The mixed-metal node effect on  $T_g$  is attributed to the difference in the degree of configurational freedom owing to the difference in tetrahedral symmetry. The degree of configurational freedom is influenced by the electronic structure and metal-nitrogen bonding nature [2]. Our study provides insight into the mixed-metal node effect on the glass transition in the HDA of ZIFs. The insight also helps design meltable ZIFs.

**Key words:** Zeolitic imidazolate frameworks; Mixed-metal node effect; High-density amorphous phases; Glass transition

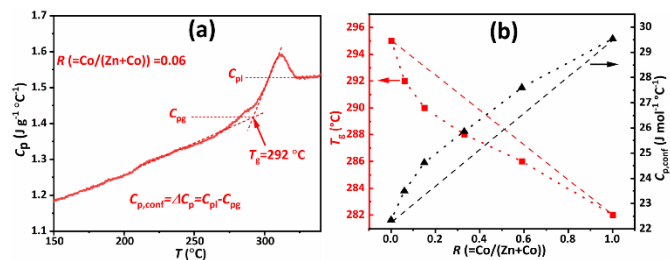


Fig. 1 (a) Isobaric heat capacity ( $C_p$ ) curve for  $Zn_{0.94}Co_{0.06}$ -HDA at the heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  in argon. (b) The molar ratio  $R$  dependence of  $T_g$  and  $C_{p,conf}$ . Dotted lines: guide for the eyes. Dashed lines: Linear lines connecting the two end-member compositions.

### References:

- [1] ANGELL C A, Science, 1995, 267, 1924-1935.
- [2] DU Z, QIAO A, ZHOU H, et al. Chem. Commun., 2023, DOI: 10.1039/D3CC02492J.
- [3] MADSEN R S K, STEPNIIEWSKA M, YANG Y, et al. RSC Adv., 2022, 12, 10815-10824.