Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

In-Situ Formation of Zeolitic-Imidazolate Framework Thin Films and Composites Using Modified Polymer Substrates

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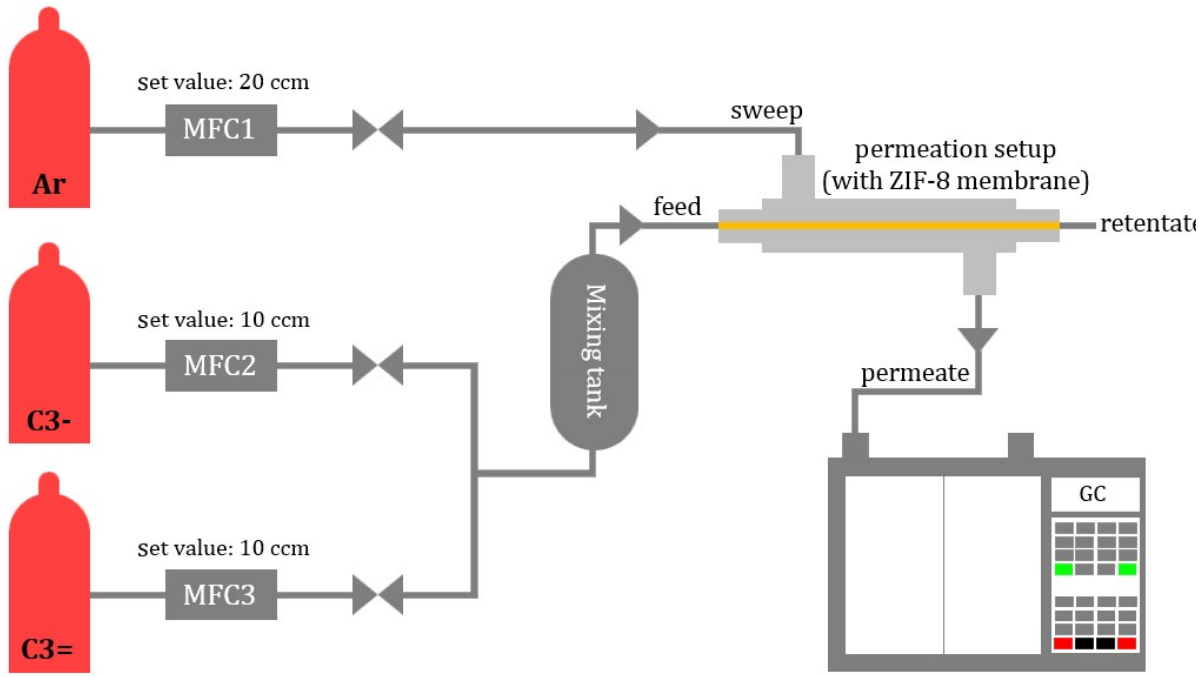
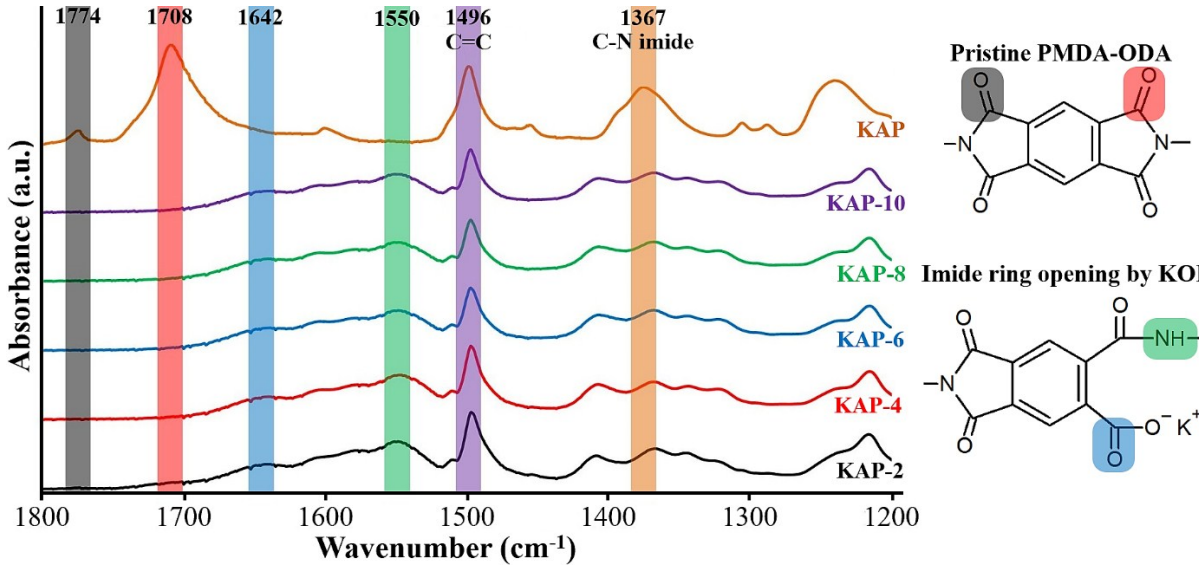


Fig. S1. Schematic illustration of the Wicke-Kallenbach set up for binary propylene/propane permeation measurements

(a)



(b)

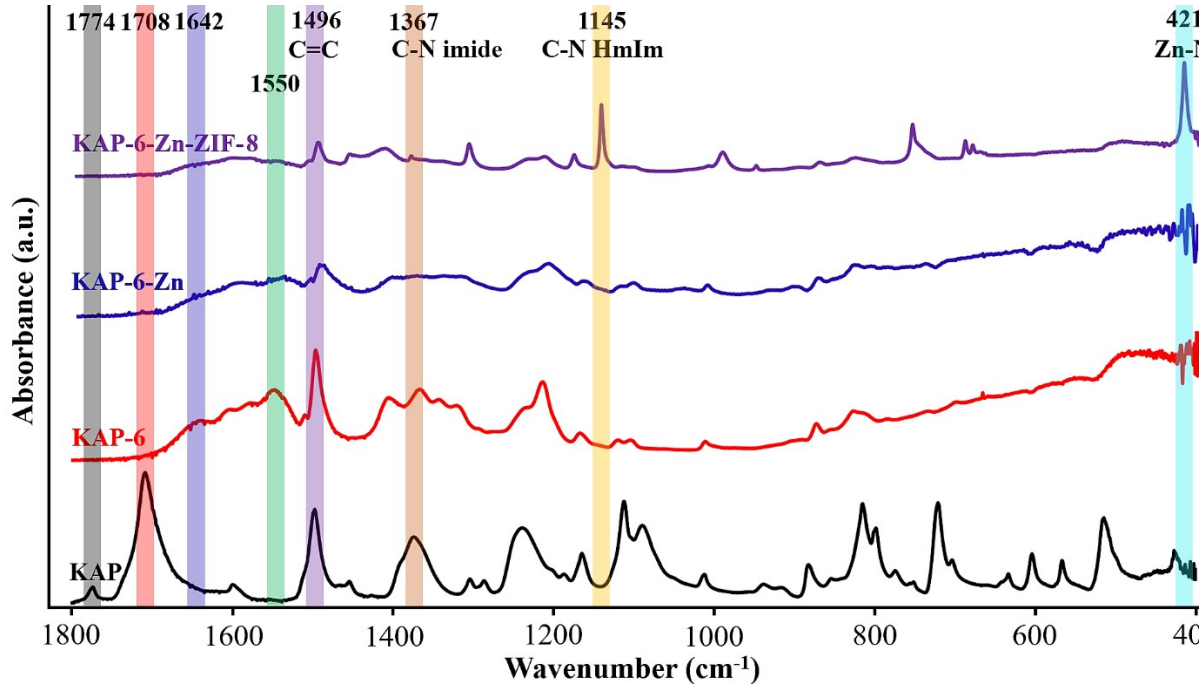


Fig. S2. (a) ATR-FTIR spectra of pristine Kapton® films (KAP) and films subjected to different hydrolysis time (KAP-x, x represents KOH treatment time in minutes) (b) ATR-

FTIR spectra of KAP, KAP-6, KAP-6-Zn, and KAP-6-Zn-ZIF-8

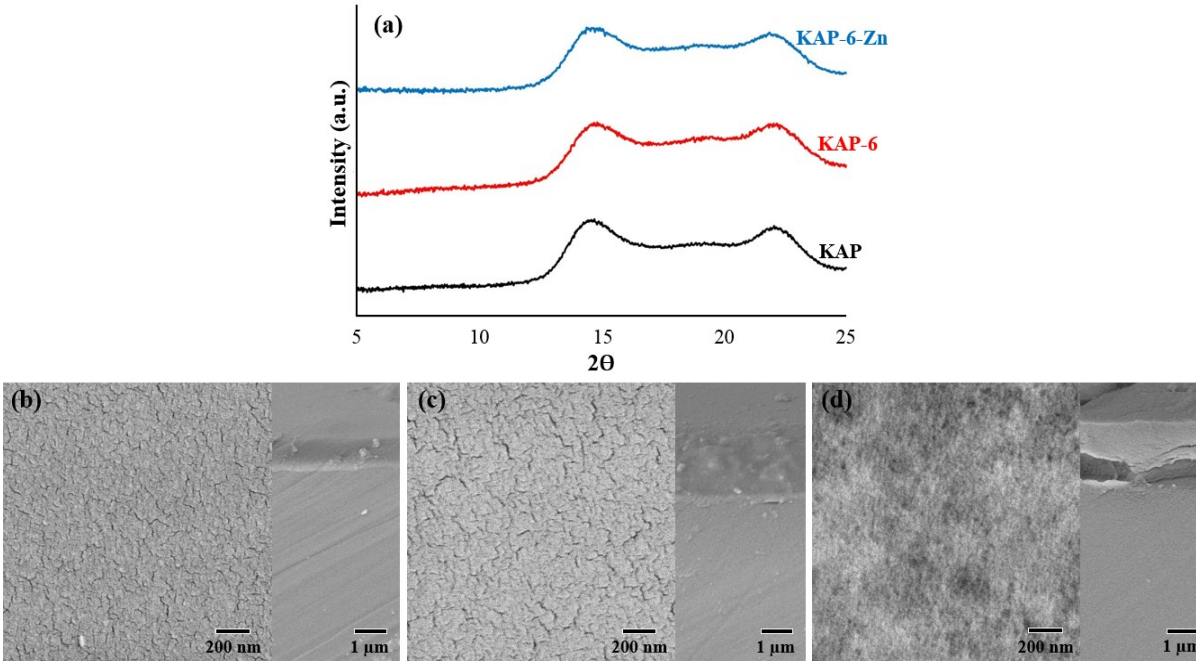


Fig. S3. (a) PXRD patterns of pristine Kapton® (KAP), 6 min KOH treated Kapton® (KAP-6), and Zn-doped Kapton® (KAP-6-Zn) films. Top and cross-sectional SEM images of (b) KAP, (c) KAP-6, and (d) KAP-6-Zn

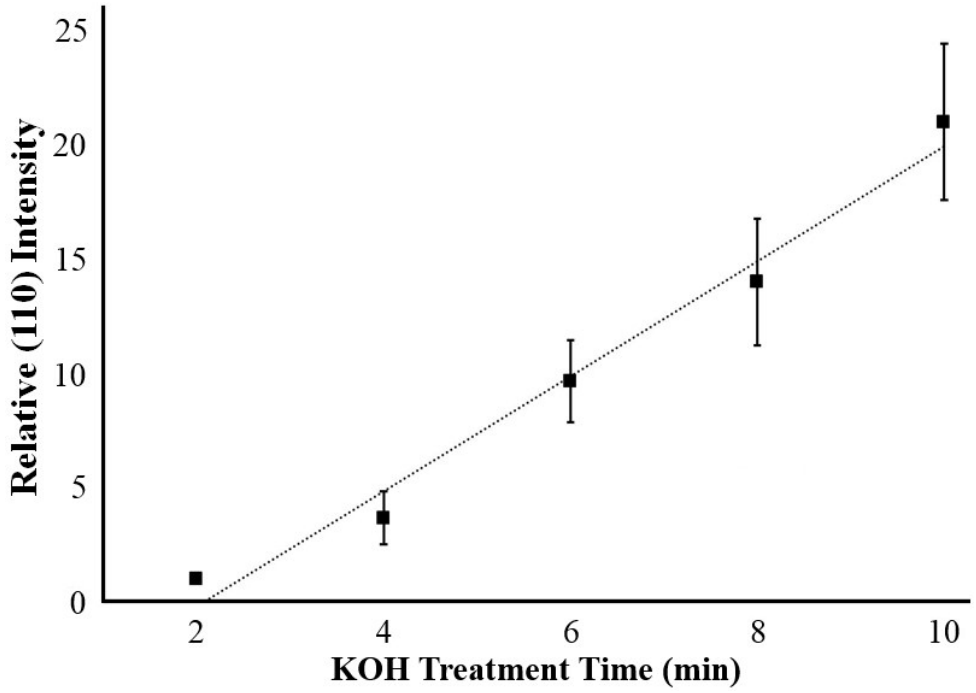


Fig. S4. Relative (110) intensity of KAP-x-Zn-ZIF-8 (x represents KOH treatment time in minutes) with respect to that of KAP-2-Zn-ZIF-8

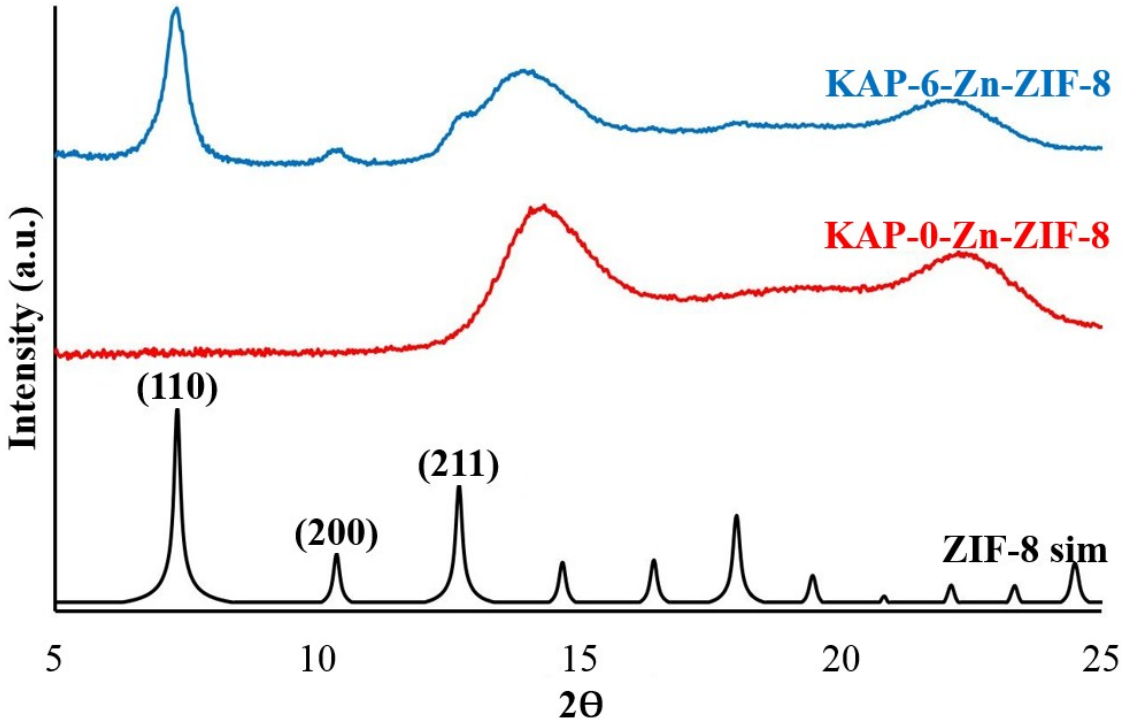
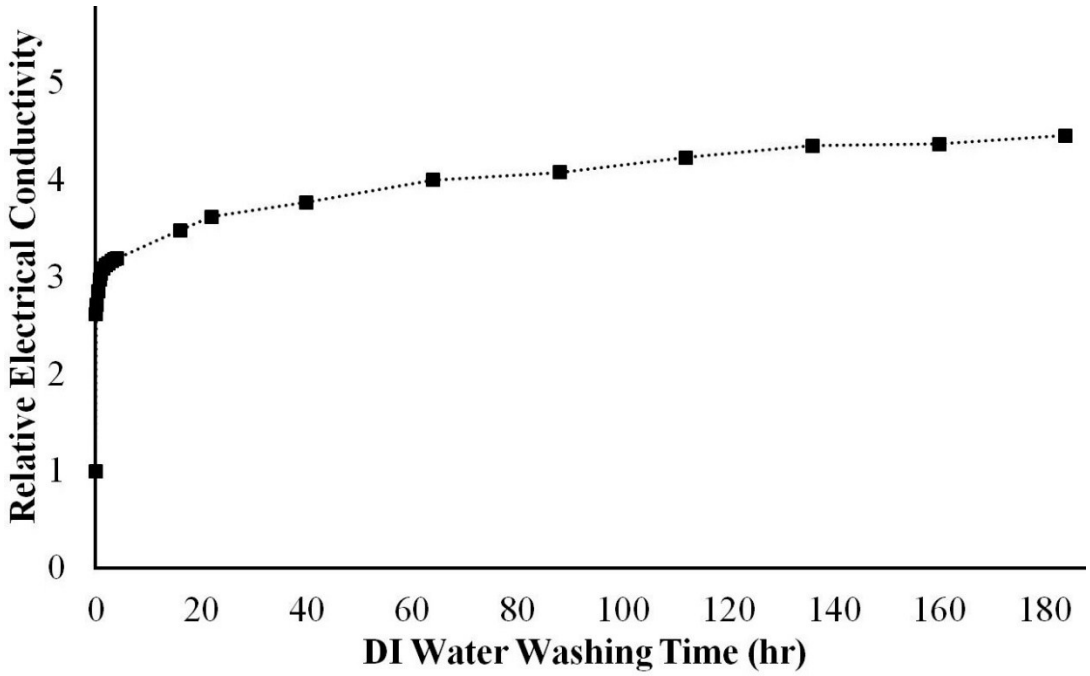


Fig. S5. PXRD pattern of a Kapton® film without KOH treatment after solvothermal reaction (KAP-0-Zn-ZIF-8) in comparison with that of a sample subjected to 6 min of KOH treatment and solvothermal reaction (KAP-6-Zn-ZIF-8)

(a)



(b)

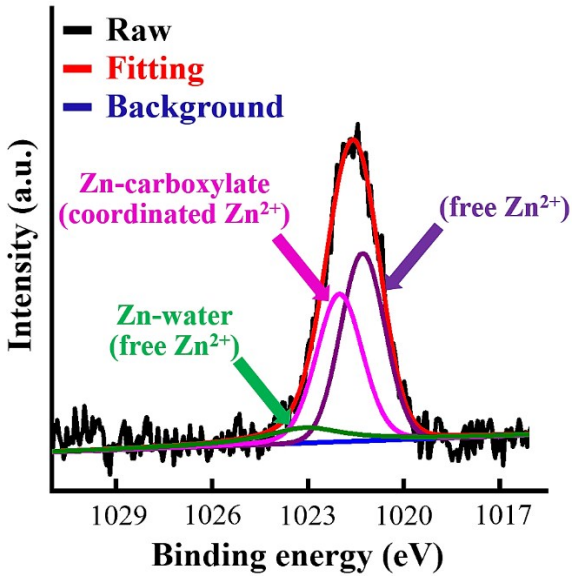


Fig. S6. (a) Relative DI water electrical conductivity ($\sigma_{t=i}/\sigma_{t=0}$) as a function of washing time and (b) high resolution XPS spectrum of the Zn^{2+}-exchanged Kapton® film after subjected to extensive washing (180 hrs.)

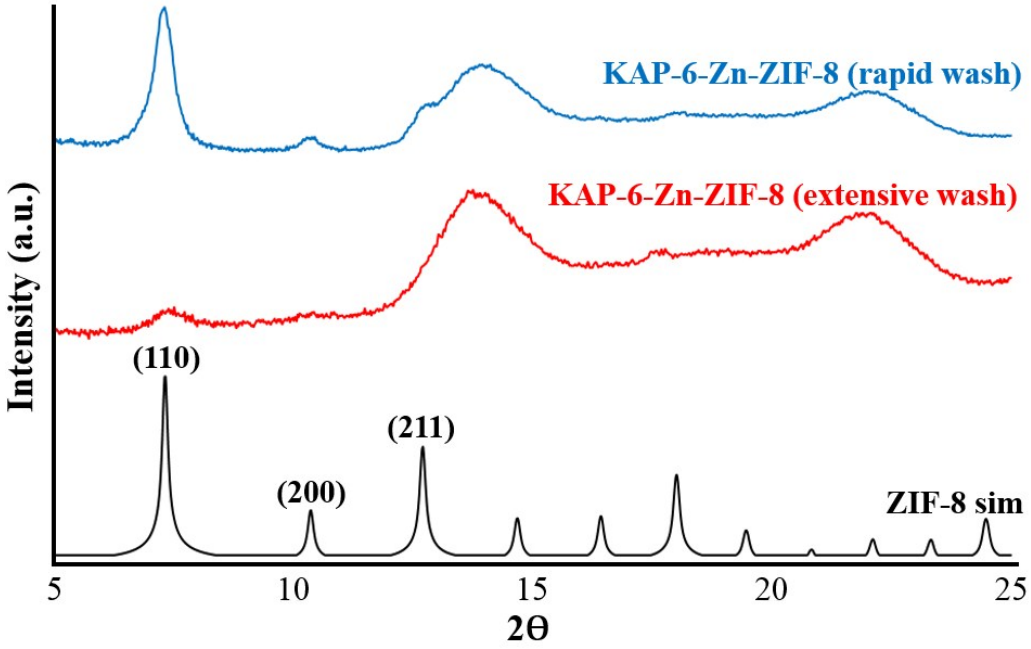


Fig. S7. PXRD patterns of samples subjected to 6 min of KOH treatment and solvothermal reaction (KAP-6-Zn-ZIF-8) after rapid and extensive washing. The Zn^{2+}-doped film with longer washing time is assumed to be free from coordinated Zn^{2+}

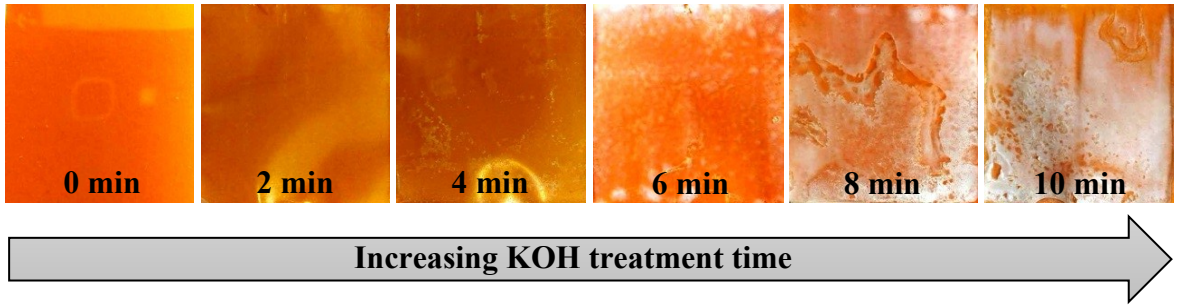


Fig. S8. Optical images of ZIF-8 thin films synthesized using Kapton® films subjected to different degree of hydrolysis

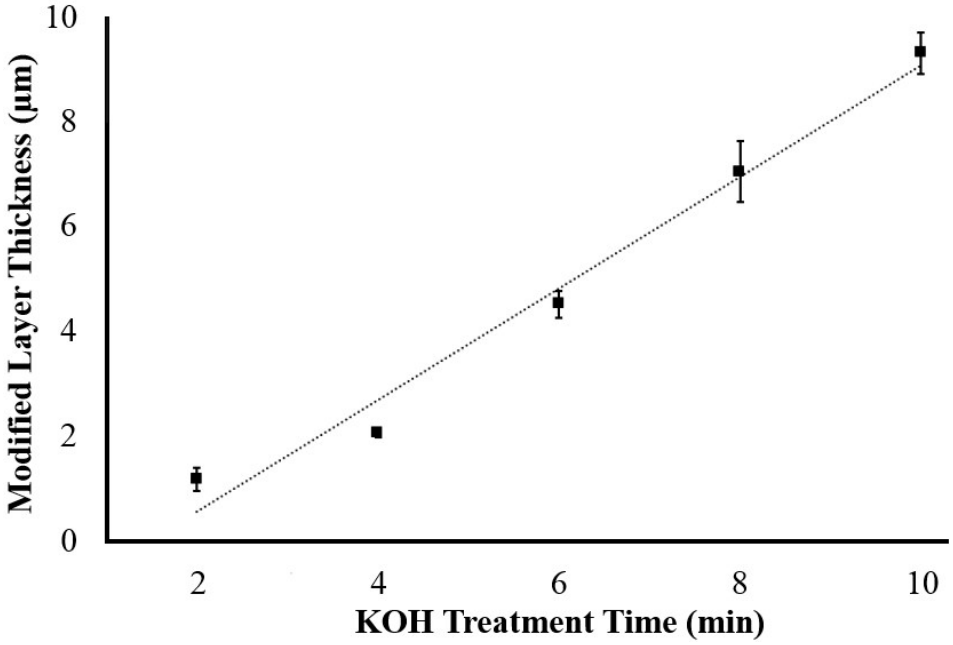


Fig. S9. Changes in ZIF-8/polymer composite layer thickness of KAP-x-Zn-ZIF-8 (x represents KOH treatment time in minutes) with respect to KOH treatment time

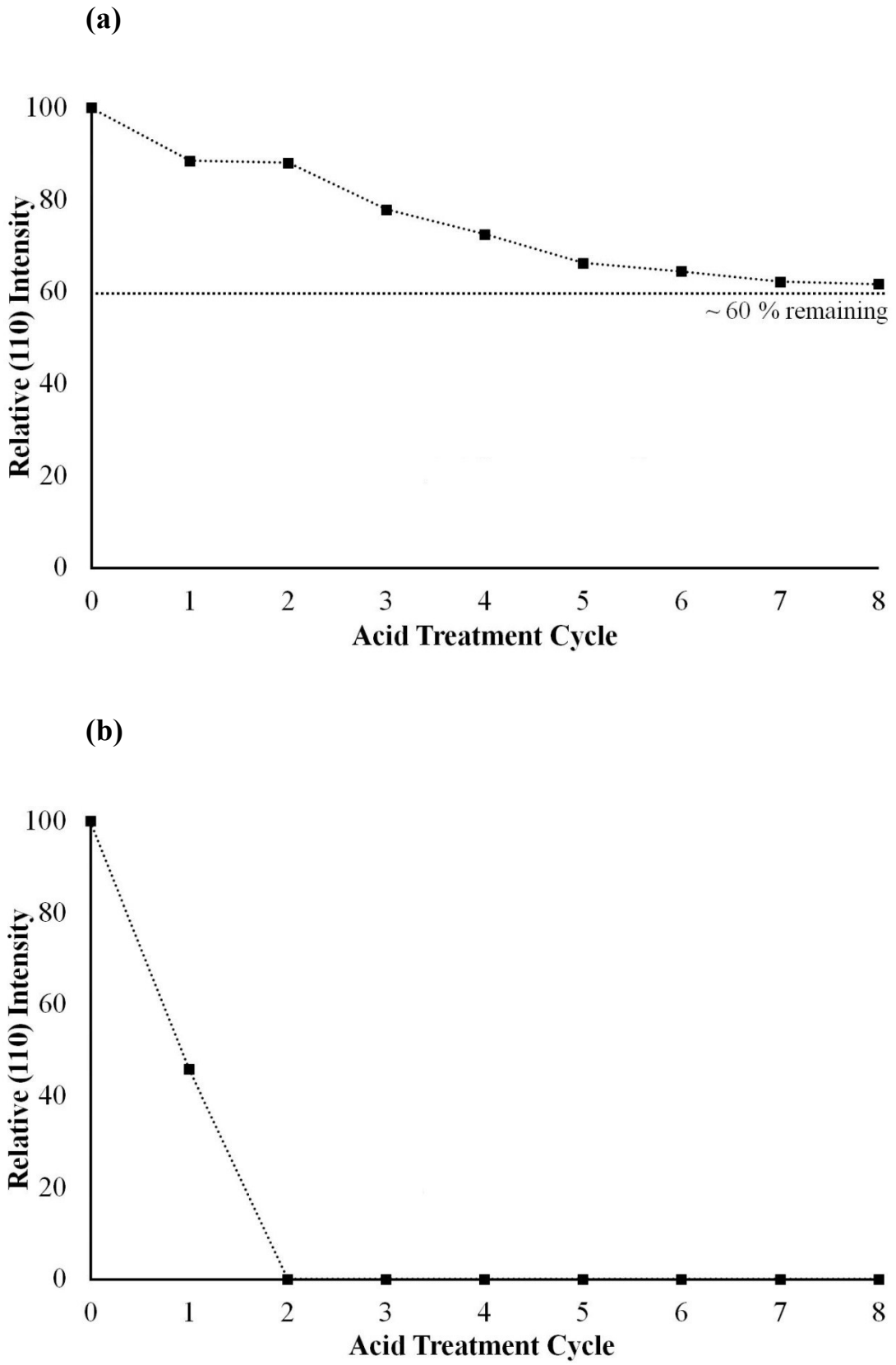
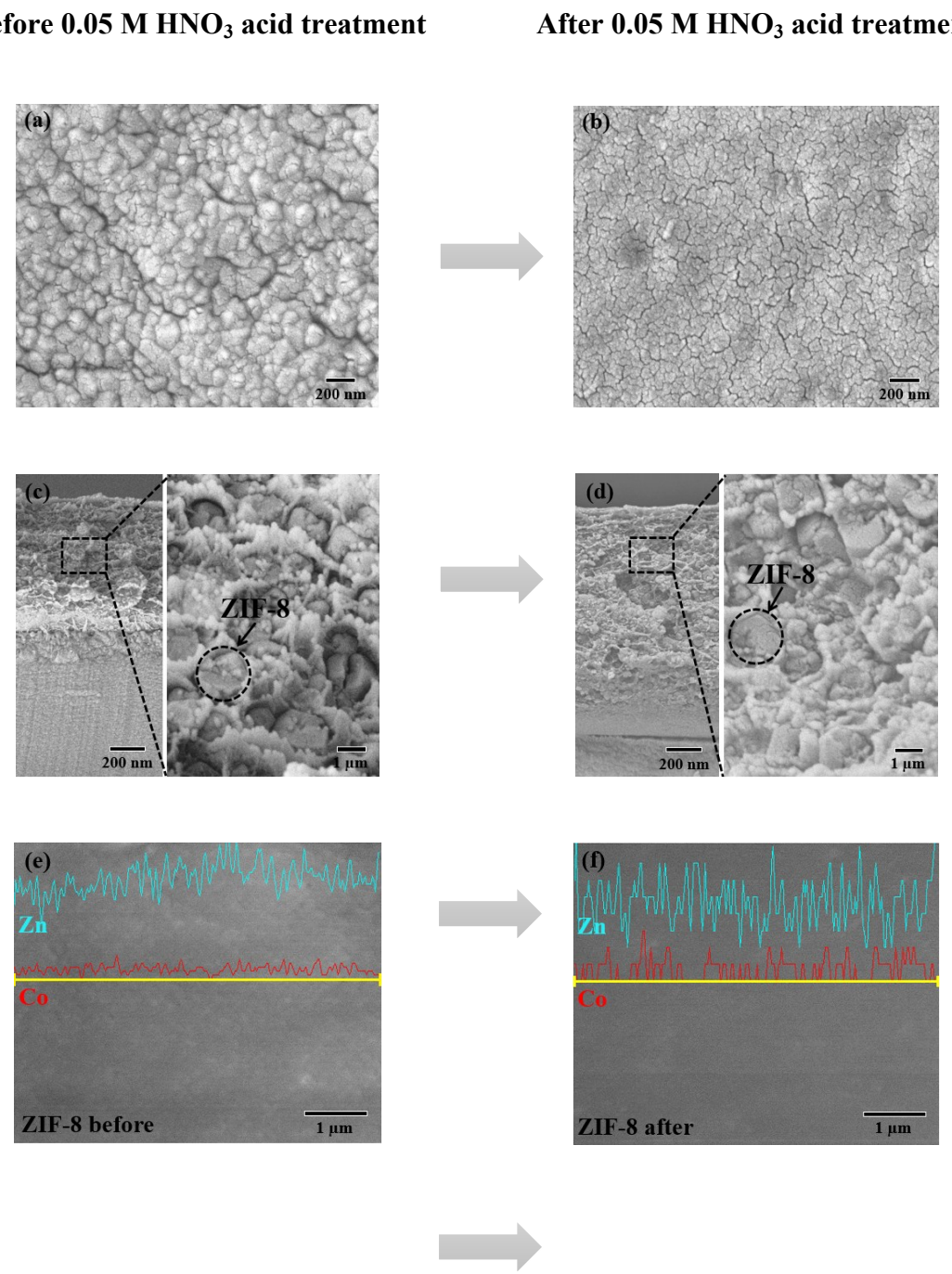


Fig. S10. Relative (110) intensity of (a) KAP-6-Zn-ZIF-8 and (b) KAP-2-Zn-ZIF-8 samples

as a function of acid treatment cycle



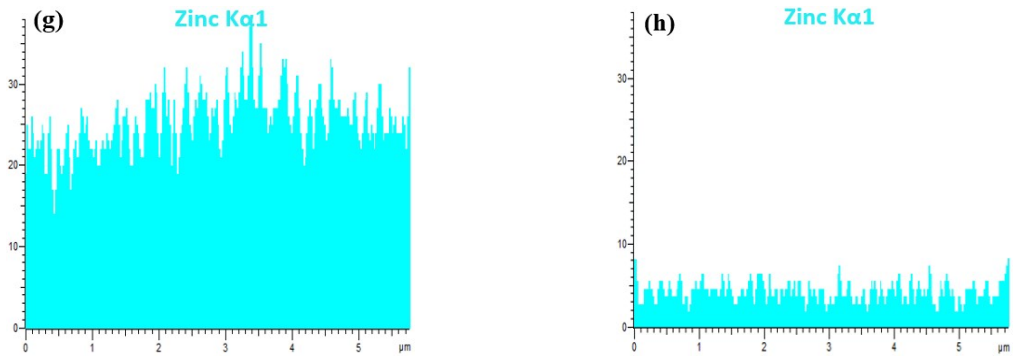


Fig. S11. (a - d) top and cross-sectional SEM images and (e - h) EDX line scan analysis of film surfaces before and after acid treatment

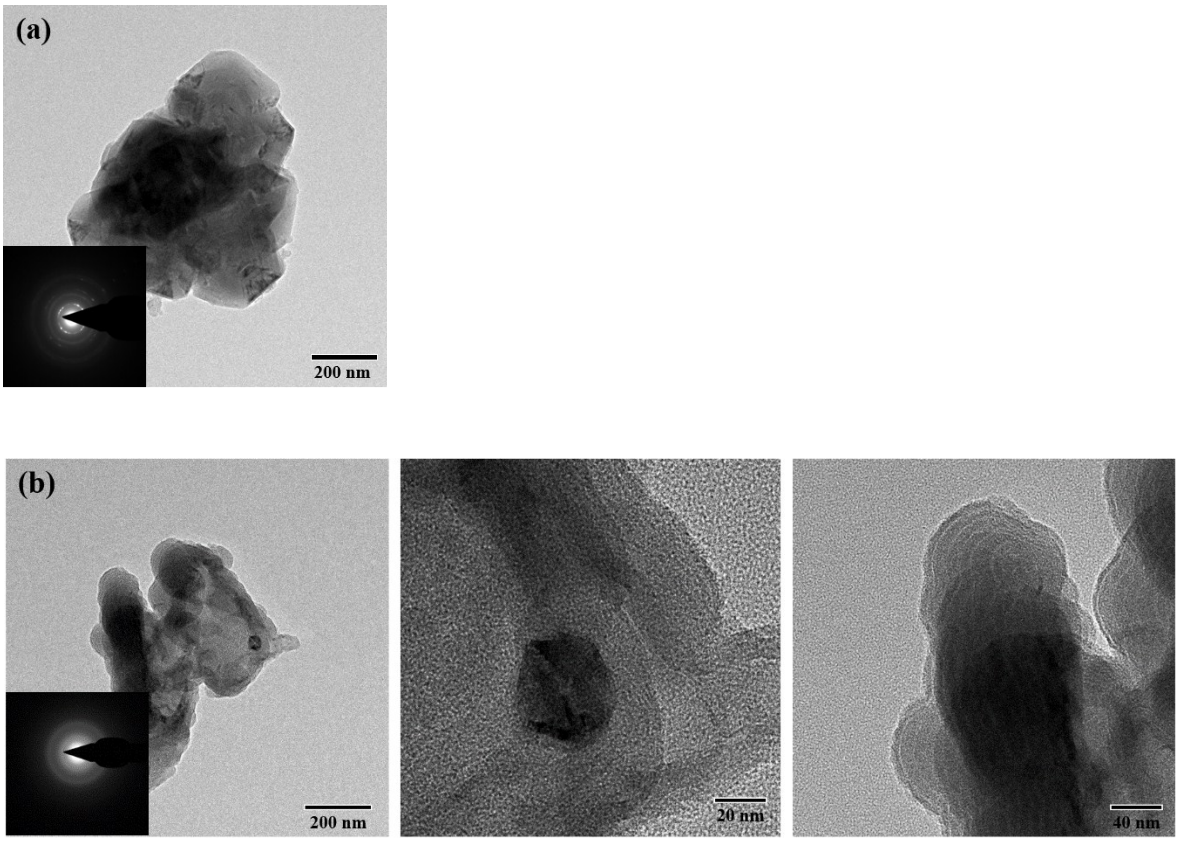


Fig. S12. Cross-sectional TEM images and electron diffraction patterns (inset) of KAP-6-Zn-ZIF-8 at (a) location A and (b) location B

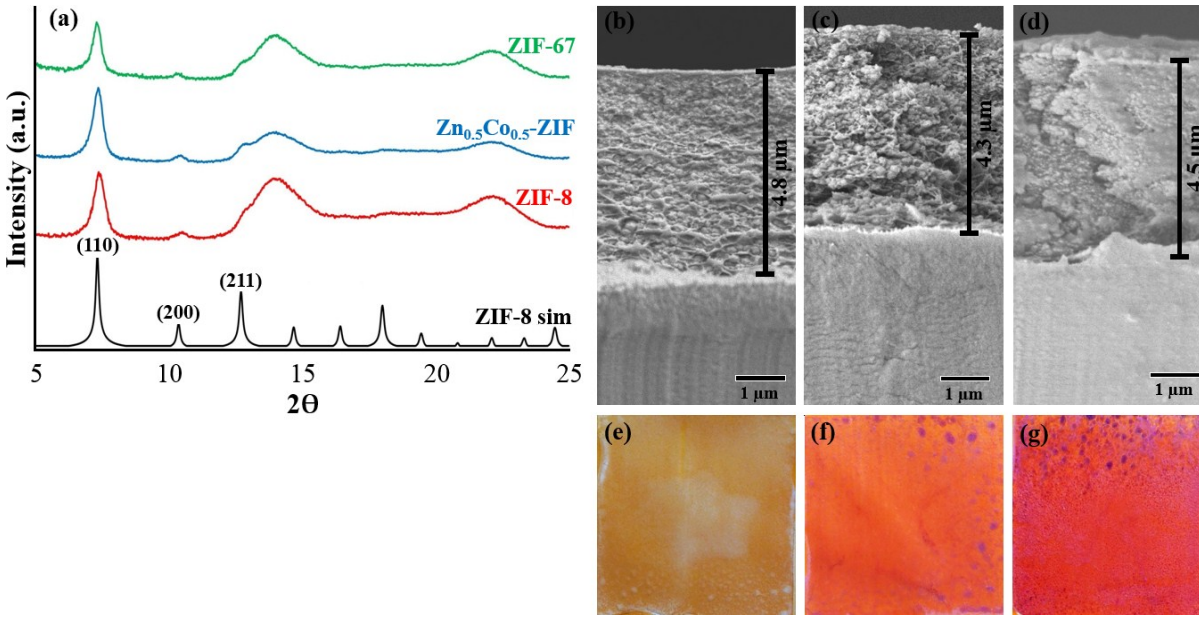


Fig. S13. (a) PXRD patterns, (b - d) cross-sectional SEM images, and (e - g) optical images of ZIF-8, $Zn_{0.5}Co_{0.5}$-ZIF-8, and ZIF-67, respectively

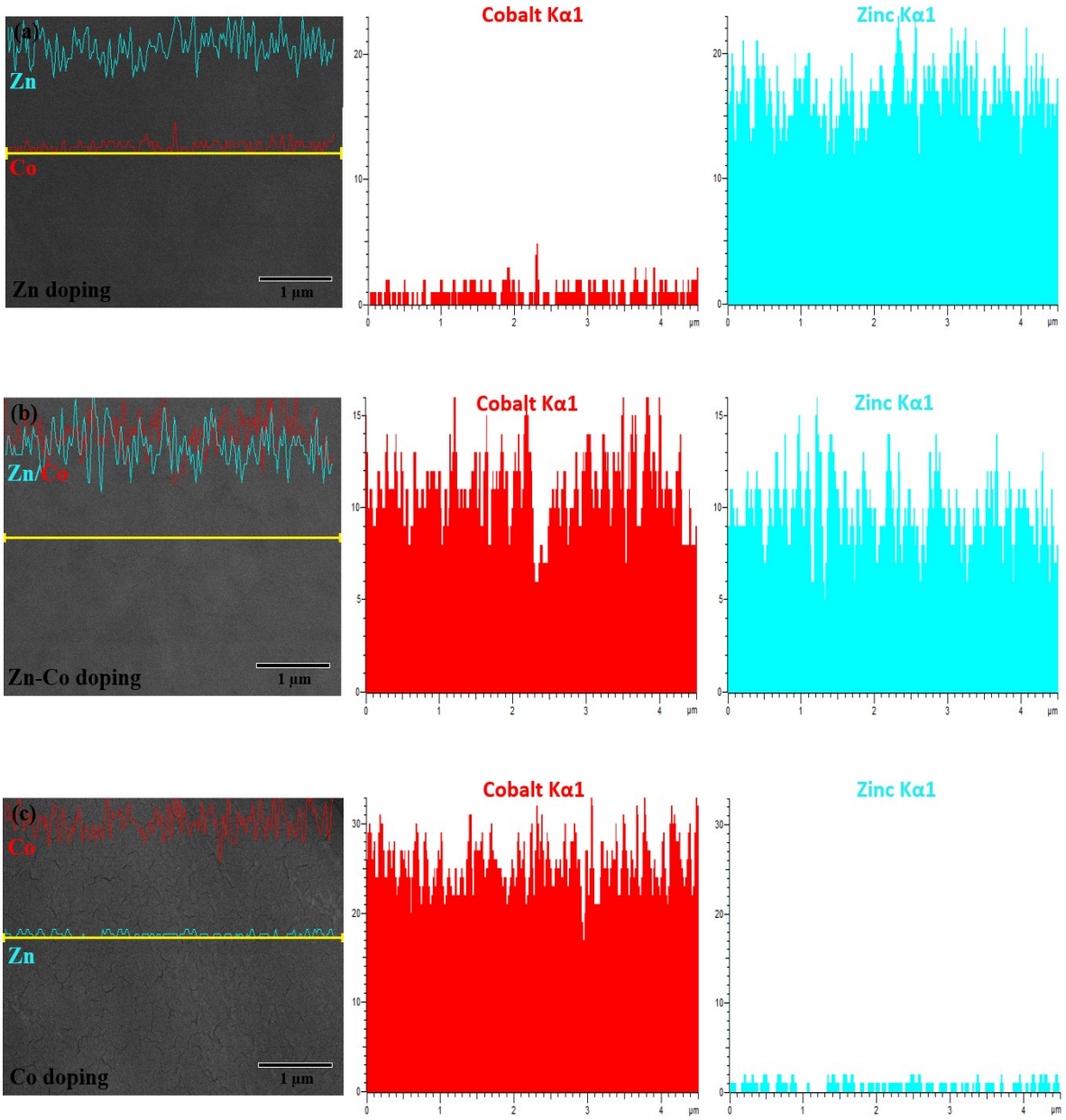


Fig. S14. EDX line profile analysis of (a) Zn^{2+}-doped, (b) $Zn_{0.5}Co_{0.5}$-doped, and (c) Co^{2+}-doped polymer substrates

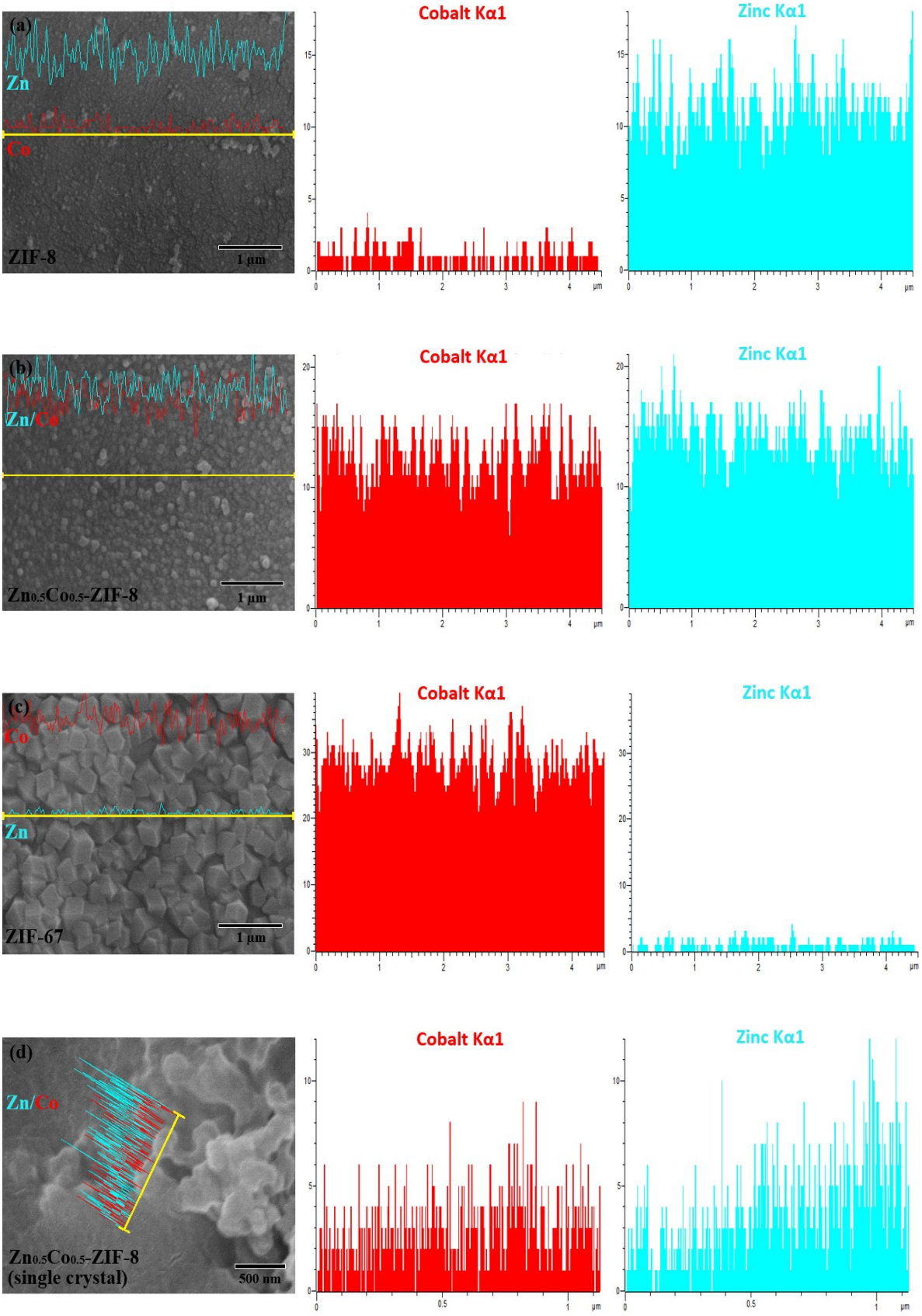


Fig. S15. EDX line profile analysis of (a) ZIF-8, (b) $Zn_{0.5}Co_{0.5}$-ZIF-8, (c) ZIF-67 thin films

on polymer substrates, and (d) $Zn_{0.5}Co_{0.5}$-ZIF-8 single crystal

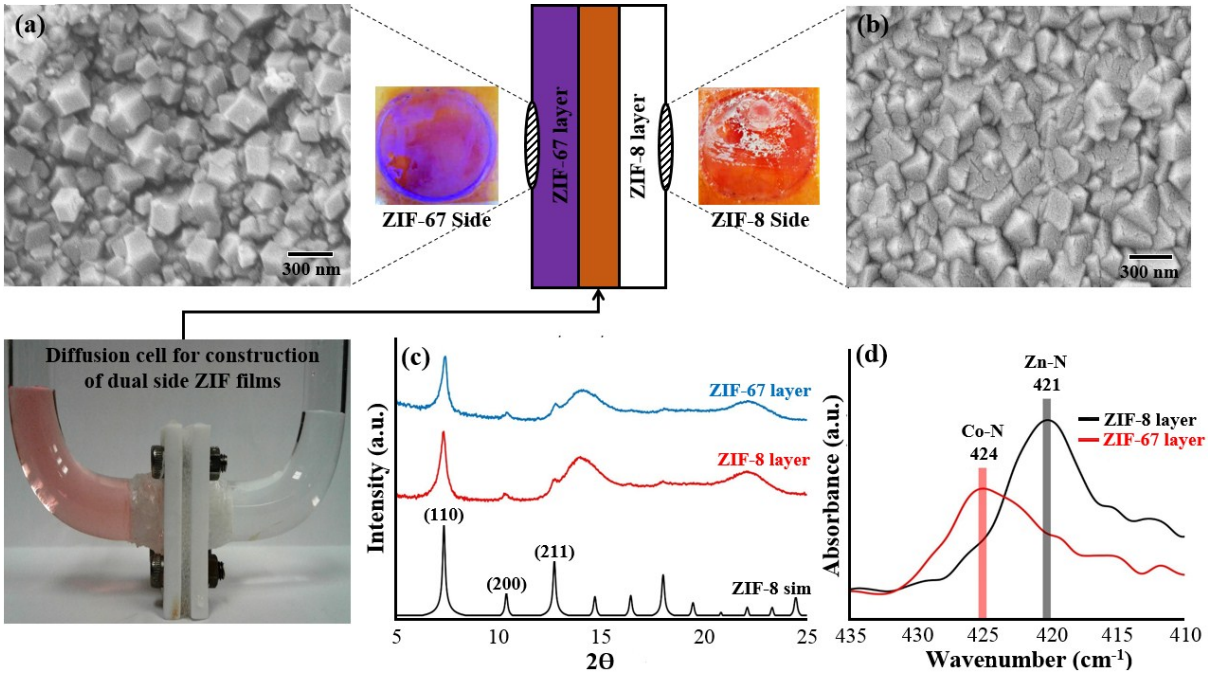


Fig. S16. Top SEM images of (a) ZIF-67 layer and (b) ZIF-8 layer, (c) PXRD patterns, and (d) ATR-FTIR spectra of ZIF-8 and ZIF-67 layers

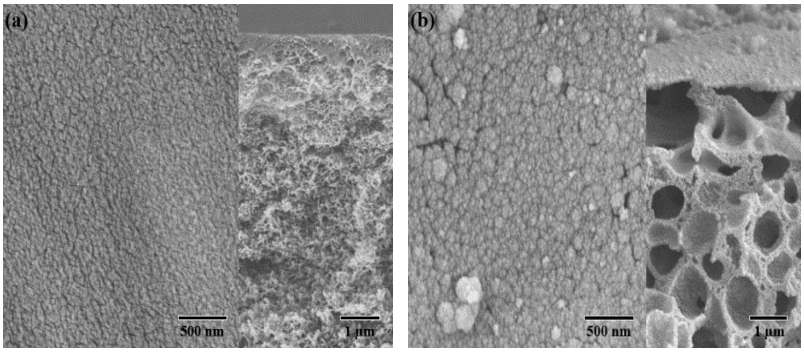


Fig. S17. Top and cross-sectional SEM images of (a) a pristine Matrimid® flat sheet and (b) a ZIF-8 thin film on a Matrimid® flat sheet substrate by the PMMOF process

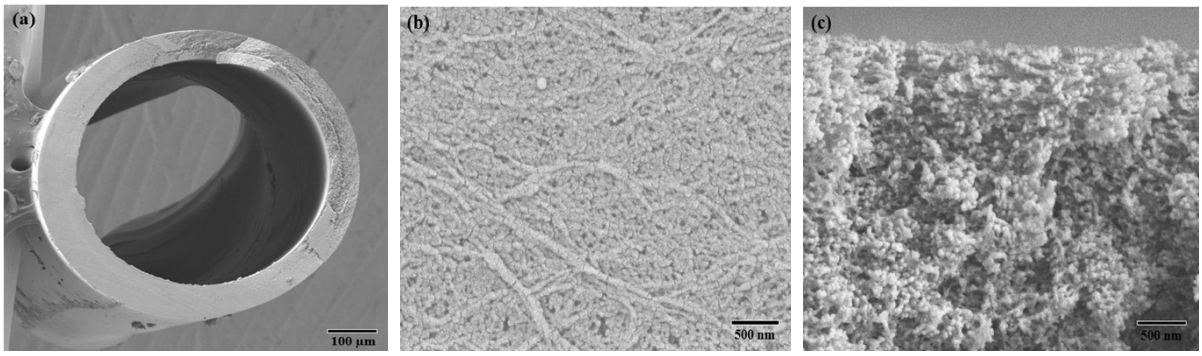


Fig. S18. (a) cross section view of a pristine Matrimid® hollow fiber under low magnification (b) top and (c) cross section view (bore side) in higher magnification

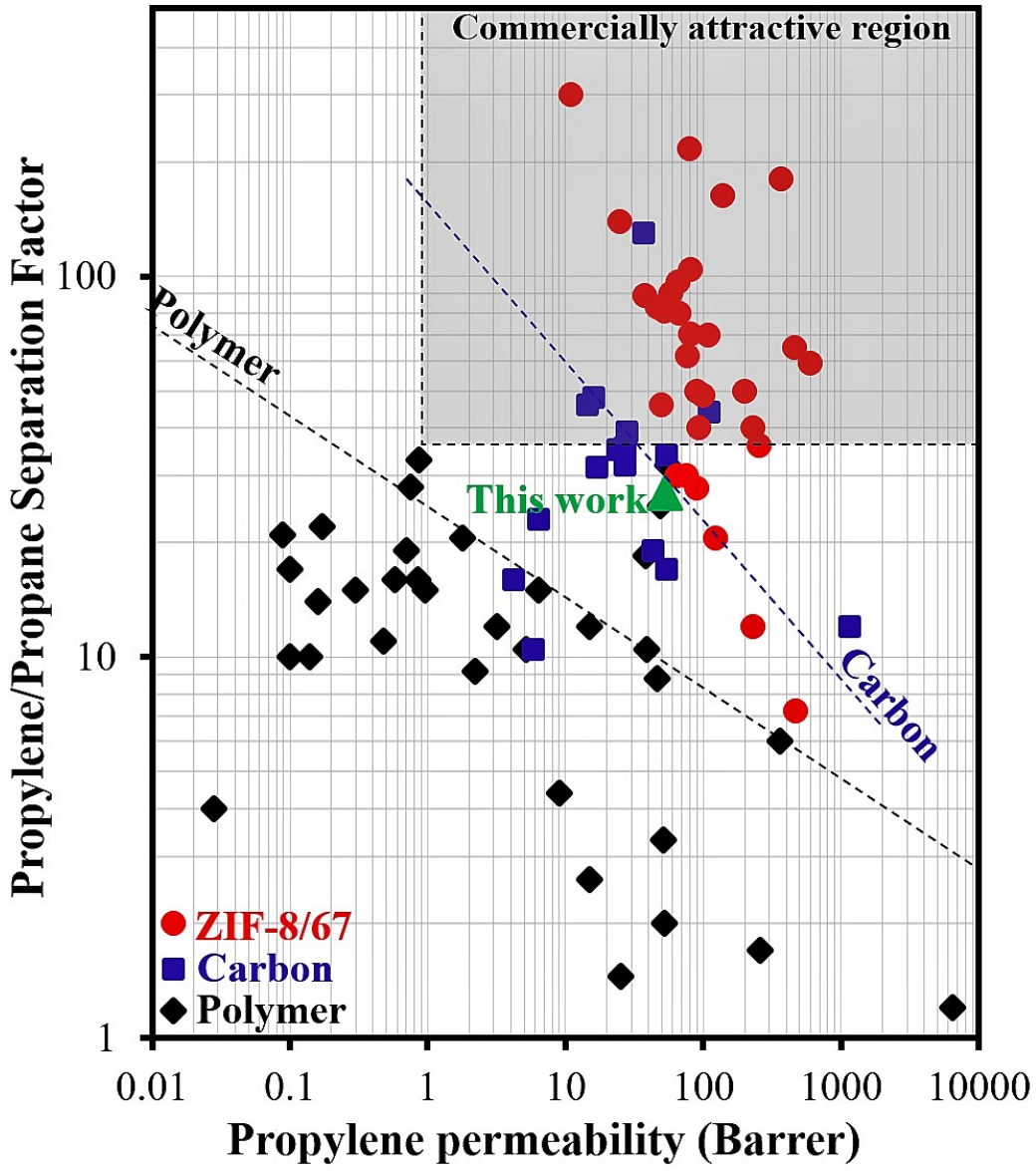


Fig. S19. Propylene/propane separation performances of the PDMS-coated ZIF-8

membranes on Matrimid® hollow fibers in comparison to those reported in literature (1 Barrer = 3.348×10^{-16} mol•m•m^{-2}•s^{-1}•Pa^{-1}). The data includes polymer [1-10], carbon [10-13], and ZIF membranes [14-38] (ZIF-8 and iso-structural ZIF-67 synthesized on either organic or inorganic substrates). Note that data for some carbon and polymer membranes are based on single gas measurements. The commercially attractive region, polymer upper bound, and carbon upper bound were drawn based on refs. [1], [13] and [39], respectively.

References

[1] R. L. Burns and W. J. Koros, J. Memb. Sci., 2003, 211, 299-309.
[2] J. Krol, M. Boerrigter and G. Koops, J. Memb. Sci., 2001, 184, 275-286.
[3] S. Bai, S. Sridhar and A. Khan, J. Memb. Sci., 1998, 147, 131-139.
[4] S. Sridhar and A. Khan, J. Memb. Sci., 1999, 159, 209-219.
[5] C. Staudt-Bickel and W. J. Koros, J. Memb. Sci., 2000, 170, 205-214.
[6] A. Shimazu, K. Ikeda and H. Hachisuka, US5749943 A.
[7] K. Tanaka, A. Taguchi, J. Hao, H. Kita and K. Okamoto, J. Memb. Sci., 1996, 121, 197-207.
[8] R. J. Swaidan, B. Ghanem, R. Swaidan, E. Litwiller and I. Pinnau, J. Memb. Sci., 2015, 492, 116-122.
[9] K. Okamoto, K. Noborio, J. Hao, K. Tanaka and H. Kita, J. Memb. Sci., 1997, 134, 171-179.
[10] K.-i. Okamoto, S. Kawamura, M. Yoshino, H. Kita, Y. Hirayama, N. Tanihara and Y. Kusuki, Ind. Eng. Chem. Res., 1999, 38, 4424-4432.
[11] M. L. Chng, Y. Xiao, T.-S. Chung, M. Toriida and S. Tamai, Carbon, 2009, 47, 1857-1866.
[12] X. Ma, B. K. Lin, X. Wei, J. Kniep and Y. Lin, Ind. Eng. Chem. Res., 2013, 52, 4297-4305.
[13] J.-i. Hayashi, H. Mizuta, M. Yamamoto, K. Kusakabe, S. Morooka and S.-H. Suh, Ind. Eng. Chem. Res., 1996, 35, 4176-4181.
[14] H. T. Kwon and H.-K. Jeong, Chem. Eng. Sci., 2015, 124, 20-26.
[15] H. T. Kwon, H.-K. Jeong, A. S. Lee, H. S. An and J. S. Lee, J. Am. Chem. Soc., 2015, 137, 12304-12311.
[16] H. T. Kwon and H.-K. Jeong, J. Am. Chem. Soc., 2013, 135, 10763-10768.
[17] Y. Pan and Z. Lai, Chem. Commun., 2011, 47, 10275-10277.
[18] H. T. Kwon and H.-K. Jeong, Chem. Commun., 2013, 49, 3854-3856.
[19] D. Liu, X. Ma, H. Xi and Y. Lin, J. Memb. Sci., 2014, 451, 85-93.
[20] Y. Pan, T. Li, G. Lestari and Z. Lai, J. Memb. Sci., 2012, 390, 93-98.
[21] F. Hillman, J. M. Zimmerman, S.-M. Paek, M. R. Hamid, W. T. Lim and H.-K. Jeong, J. Mater. Chem. A, 2017, 5, 6090-6099.

[22] N. Hara, M. Yoshimune, H. Negishi, K. Haraya, S. Hara and T. Yamaguchi, J. Memb. Sci., 2014, 450, 215-223.
[23] K. Huang, B. Wang, Y. Chi and K. Li, Adv. Mater. Interfaces, 2018, 5, 1800287.
[24] J. Sun, C. Yu and H.-K. Jeong, Crystals, 2018, 8, 373.
[25] W. Li, P. Su, Z. Li, Z. Xu, F. Wang, H. Ou, J. Zhang, G. Zhang and E. Zeng, Nat. Commun., 2017, 8, 406.
[26] A. J. Brown, N. A. Brunelli, K. Eum, F. Rashidi, J. Johnson, W. J. Koros, C. W. Jones and S. Nair, Science, 2014, 345, 72-75.
[27] K. Eum, A. Rownaghi, D. Choi, R. R. Bhave, C. W. Jones and S. Nair, Adv. Funct. Mater., 2016, 26, 5011-5018.
[28] M. J. Lee, M. R. A. Hamid, J. Lee, J. S. Kim, Y. M. Lee and H.-K. Jeong, J. Memb. Sci., 2018, 559, 28-34.
[29] E. Shamsaei, X. Lin, Z.-X. Low, Z. Abbasi, Y. Hu, J. Z. Liu and H. Wang, ACS Appl. Mater. Interfaces, 2016, 8, 6236-6244.
[30] N. Hara, M. Yoshimune, H. Negishi, K. Haraya, S. Hara and T. Yamaguchi, Microporous Mesoporous Mater., 2015, 206, 75-80.
[31] M. J. Lee, H. T. Kwon and H. K. Jeong, Angew. Chem., 2018, 130, 162-167.
[32] M. J. Lee, H. T. Kwon and H.-K. Jeong, J. Memb. Sci., 2017, 529, 105-113.
[33] Y. Pan, W. Liu, Y. Zhao, C. Wang and Z. Lai, J. Memb. Sci., 2015, 493, 88-96.
[34] C. Wang, F. Yang, L. Sheng, J. Yu, K. Yao, L. Zhang and Y. Pan, Chem. Commun., 2016, 52, 12578-12581.
[35] S. Zhou, Y. Wei, L. Li, Y. Duan, Q. Hou, L. Zhang, L.-X. Ding, J. Xue, H. Wang and J. J. S. a. Caro, Sci. Adv., 2018, 4, eaau1393.
[36] J. H. Lee, D. Kim, H. Shin, S. J. Yoo, H. T. Kwon and J. Kim, J. Ind. Eng. Chem., 2018.
[37] S. Tanaka, K. Okubo, K. Kida, M. Sugita and T. Takewaki, J. Memb. Sci., 2017, 544, 306-311.
[38] L. Sheng, C. Wang, F. Yang, L. Xiang, X. Huang, J. Yu, L. Zhang, Y. Pan and Y. Li, Chem. Commun., 2017, 53, 7760-7763.
[39] C. W. Colling, G. A. Huff Jr and J. V. Bartels, US 20040004040 A1.