# Supporting Information

## Copolymers with Tailored Microstructure as Versatile Platforms for ZIF-8 PolyMOF Growth

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**Synthesis of BrPTES:**

A volume of 42 mL of dry dichloromethane ($CH_2Cl_2$) was used to dissolve 3-aminopropyltrimethoxysilane (APTES) (9.03 mmol; 1.6 mL) and triethylamine (11.14 mmol; 1.55 mL). The system is gradually cooled to 0 °C while bubbling with $N_2$ for 30 min to create an inert atmosphere. In a 10 mL vial, 1.12 mL of α-bromoisobutyryl bromide dissolved in dichloromethane to give a solution of approximately 50 % v/v concentration. This solution was syringed and dripped into the balloon through the septum, maintaining the $N_2$ atmosphere throughout the addition. The solution was left to react until the next day to allow cooling down until constant temperature.

The next day the solution was filtered, and the organic phase was washed with brine and distilled water until a neutral pH was reached. Finally, it was transferred to a rotary

evaporator to remove the organic solvent residues. Yield: 1.89 g (59 %). 1H NMR (500 MHz, $CDCl_3$), Figure S1.

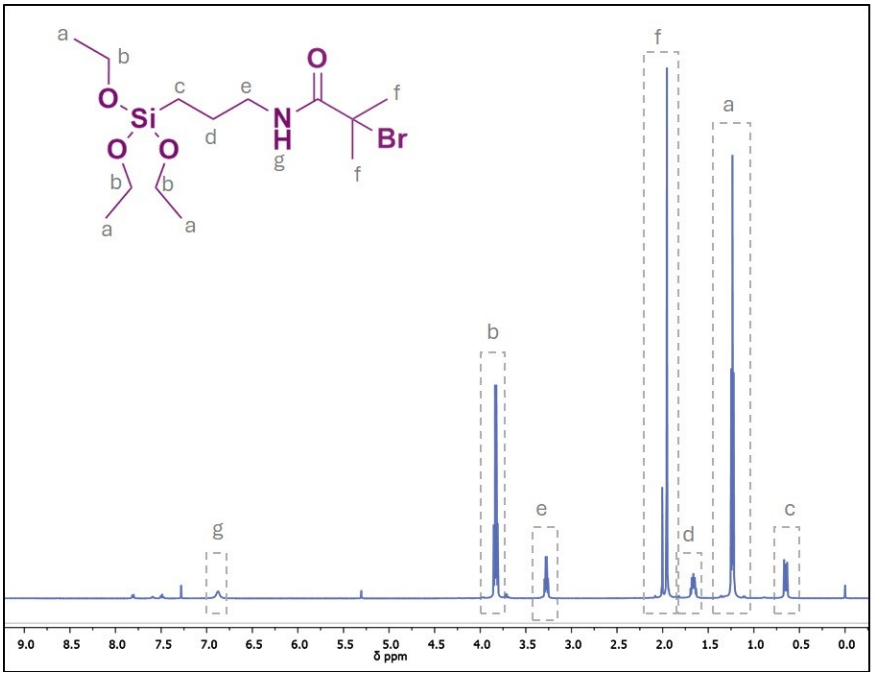


**Figure S1:** BrPTES structure and their 1H NMR spectra.

**Synthesis of ZIF-8 in bulk:**

ZIF-8 was synthesized according to previously reported by Allegretto et al.[1] and as detailed in the Supplementary Information. An anhydrous methanolic solution of $Zn(NO_3)_2.6H_2O$ (25 mM) was prepared, and after a few minutes, an equal volume of 50 mM HmIm in anhydrous methanol was added. After a reaction time of 30 min, the precipitated material was centrifuged at 11.000 rpm, washed thoroughly with methanol, and subsequently dried under vacuum at 80 °C. The obtained material was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) to evaluate its crystalline structure and morphology. Yield: 92 mg (10 %). Main diffraction peaks observed consistent with the ZIF-8 structure, Figure S2.

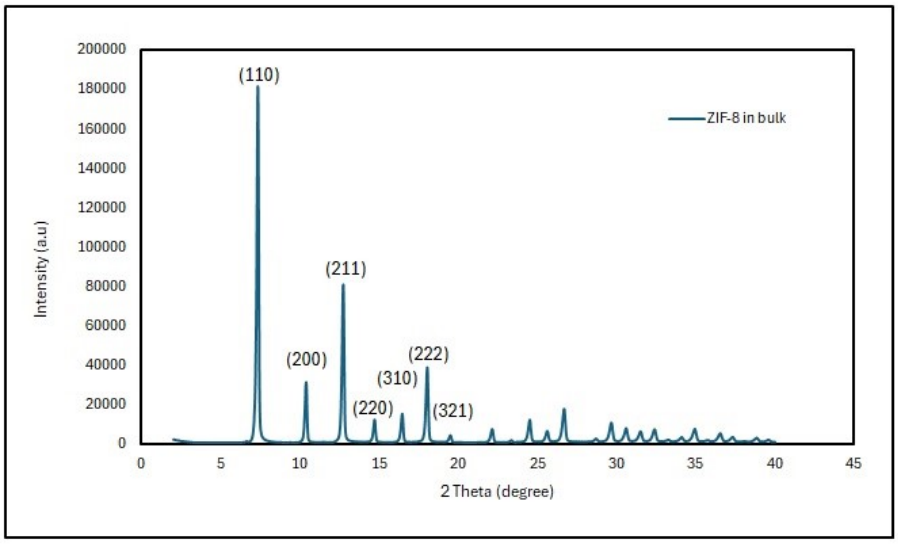


**Figure S2:** XRD pattern of ZIF-8.

**Raman, XPS, XRD and SEM Analysis of Surface-Grafted PolyMOFs:**

Surface-grafted poly(ZDMAx-*co*-PEGMAy) copolymers were used to prepare poly(ZDMAx-*co*-PEGMAy)@ZIF-8-surface polyMOFs. Figure S3A displays the XPS spectra, while Figure S3B shows the corresponding XRD pattern. XPS signals in the N1s region indicated reduced oxidation damage as the composite layer became more complex, transitioning from BrAPTES-coated substrates to surface-grown polyMOFs.

PolyMOF formation is strongly influenced by the composition of poly(ZDMAx-*co*-PEGMAy) brushes. At low $f_{ZnDMA}$ values, XRD analysis revealed limited or no crystalline peaks, suggesting an insufficient density of nucleation sites on the surface-grafted copolymer. Optimal growth and crystallinity were achieved at intermediate $f_{ZnDMA}$ values, whereas excessive $Z_{nDMA}$ content resulted in reduced crystallinity. This loss of order may be attributed to over-nucleation, the development of amorphous phases, or kinetic hindrance caused by excessive coordination.

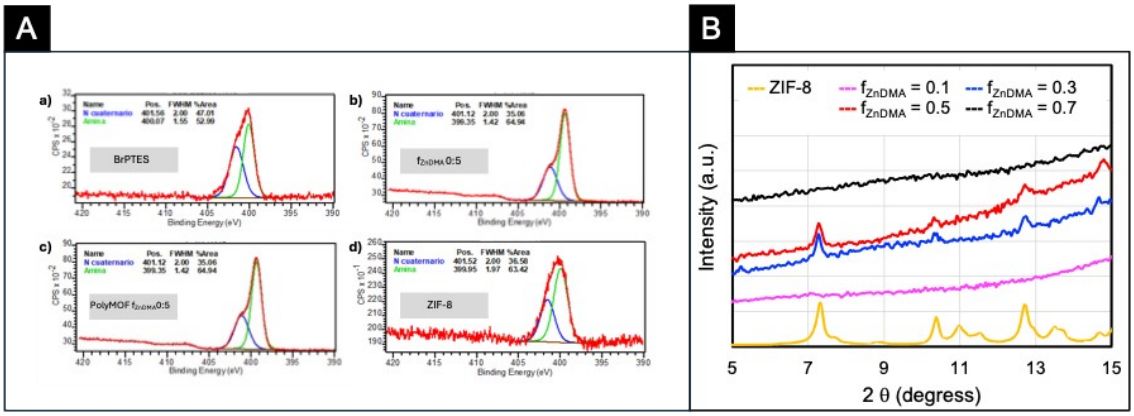


**Figure S3:** (A) XPS spectra and (B) XRD pattern of poly(ZDMAx-co-PEGMAy)@ZIF-8 -surface.

Signals in Raman spectra shown in Figure S4 were assigned as they correspond to the corresponding monomers, glass substrate or copolymer anchor initiatior BrAPTES (1400 $cm^{-1}$ and 2900 - 3000 $cm^{-1}$ for PEGMA, 200 $cm^{-1}$ and 700 – 800 $cm^{-1}$ for ZnDMA, 600 $cm^{-1}$ and 1100 $cm^{-1}$ for substrate and initiator). To determine monomer composition in surface grafted copolymers, calibration curves were obtained adding fixed amounts of monomers to clean substrates.

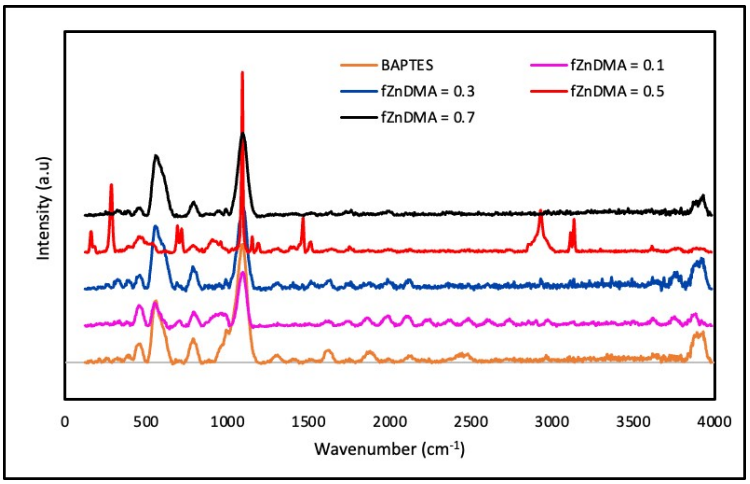


**Figure S4:** Raman spectra of poly(ZDMAx-co-PEGMAy) -surface.

SEM analysis shown in Figure S5 includes images corresponding to the intermediate compositions ($f_{ZnDMA}$ = 0.3 and 0.5), as well as bulk ZIF-8 and ZIF-8 on glass.

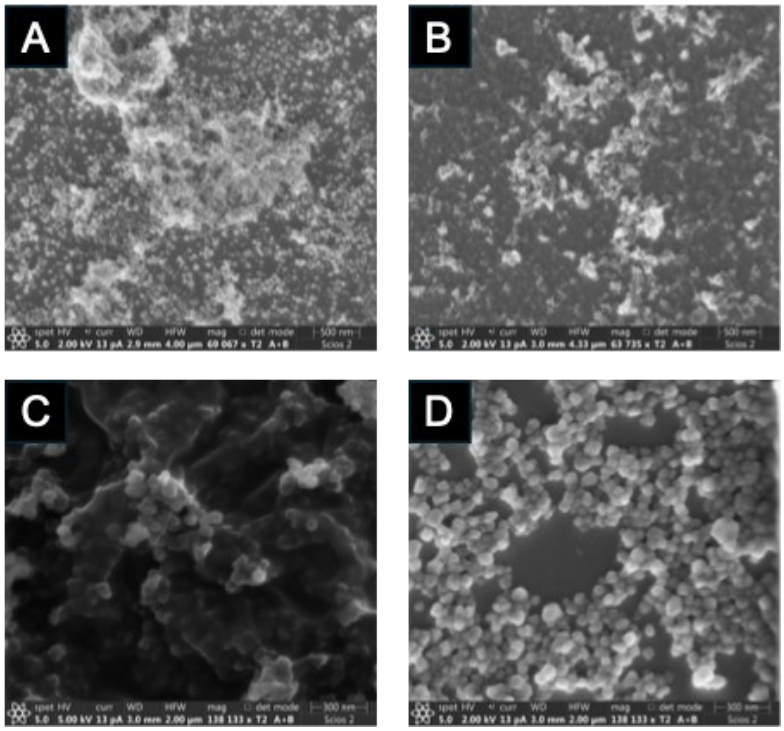


**Figure S5:** (A to B) SEM image of surface grafted PolyMOF on poly(ZnDMA-co-PEGMA)@ZIF8-surface with 0.3 and 0.5 $f_{ZnDMA}$. (C) bulk ZIF-8. (D) ZIF-8 on glass.

## Cristalinity Analysis by HR-TEM

For polyMOF samples, lattice-plane distances were estimated from HR-TEM images, yielding values of 1.6 ± 0.2 nm. These values are consistent with the reported ~1.16 nm lattice-plane distance for ZIF-8, based on its theoretical pore size and in agreement with previously reported HR-TEM measurements of ZIF-8 nanostructures (Hugenschmidt et al.[2]). The observed differences may be attributed to variations in pore size related to the polymer scaffold. In contrast, the estimated values differ significantly from Zn and ZnO, which exhibit lattice parameters of approximately 0.2–0.3 nm. Taken together, these results confirm that the polyMOF possesses a crystalline structure, which may be partially obscured by the high amorphous polymer content.

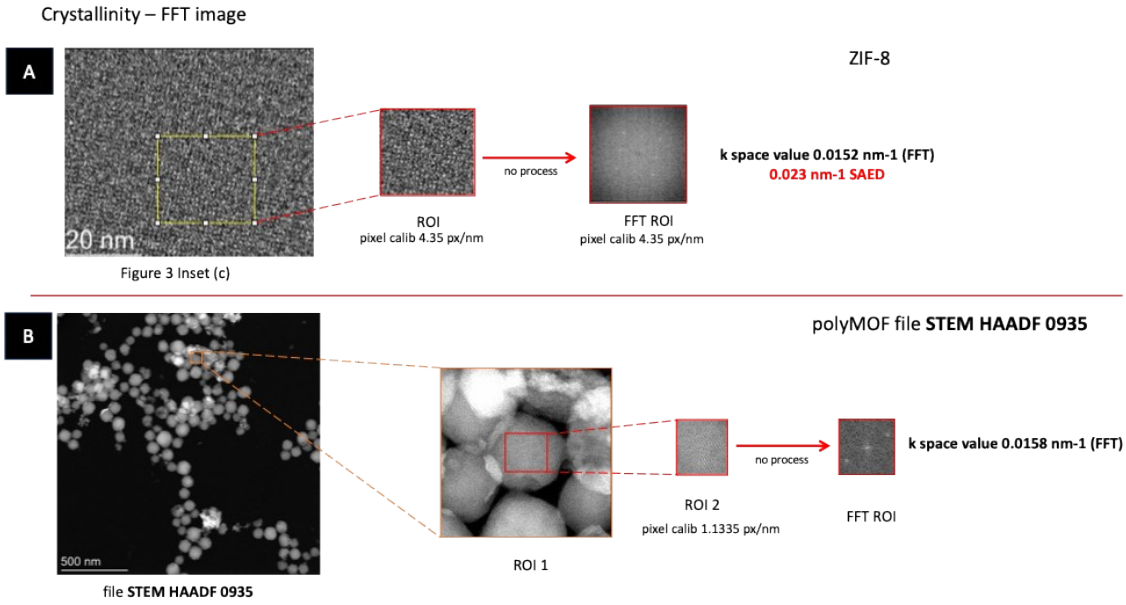


**Figure S6:** HR-TEM images showing lattice-plane distances. (A) Reference HR-TEM image of ZIF-8 reported by Hugenschmidt et al., used for comparison. (B) HR-TEM image of poly(ZDMAx-co-PEGMAy)@ZIF-8 (bulk).

## REFERENCES

[1] Allegretto JA, Iborra A, Giussi JM, von Bilderling C, Ceolín M, Moya S, et al. Growth of ZIF-8 MOF Films with Tunable Porosity by using Poly (1-vinylimidazole) Brushes as 3D Primers, *Chemistry - A European Journal*, 2020, **26**, 12388-12396.

[2] Hugenschmidt M, Kutonova K, Valadez Sánchez EP, Moulai S., Gliemann H., Bräse S., Wöl C. and Gerthsen D. Direct Synthesis of ZIF-8 on Transmission Electron Microscopy Grids Allows Structure Analysis and 3D Reconstruction, *Partycles Systems and Characterization*, 2020, **37**, 2000209.