

**Supporting information for**

**Etching and Polymerization Reactions of Alkoxythiophenes in HKUST-1: Choosing Between Filled and Core-Shell MOF/Polymer Composite Structures**

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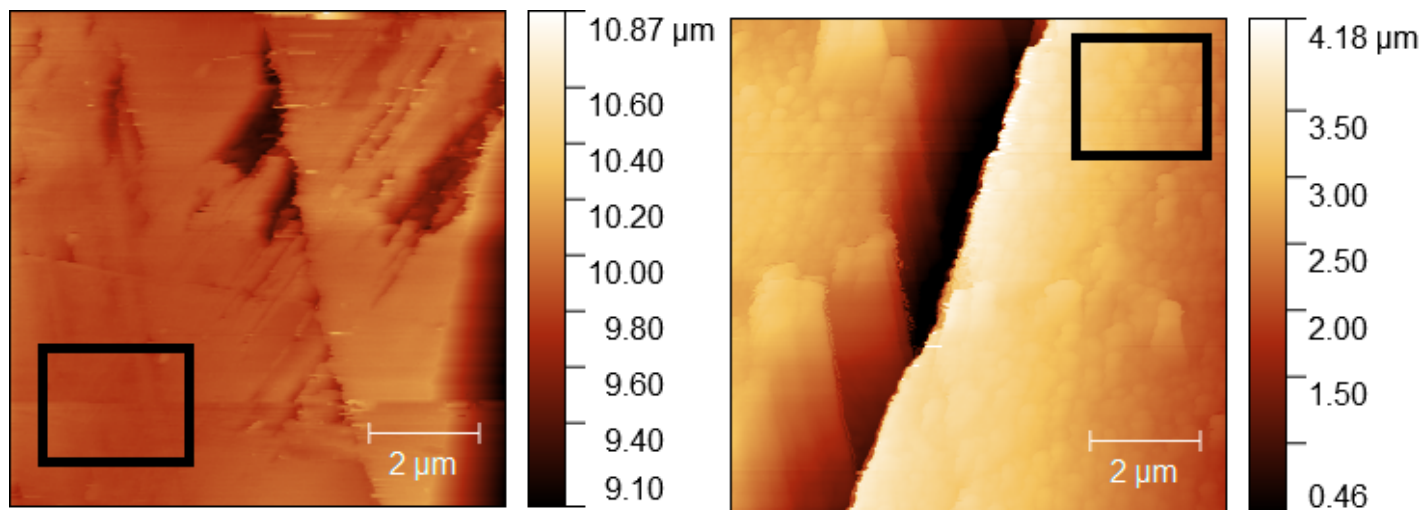


Figure S1. Hexane-loaded PEDOT in HKUST-1 (left) shows roughening due to etching, but no surface polymer (rms roughness = 33 nm). However, the composite prepared from the neat EDOT monomer (right) has substantial polymer nodules (rms roughness = 320 nm). Roughnesses are calculated in the regions indicated by black boxes.

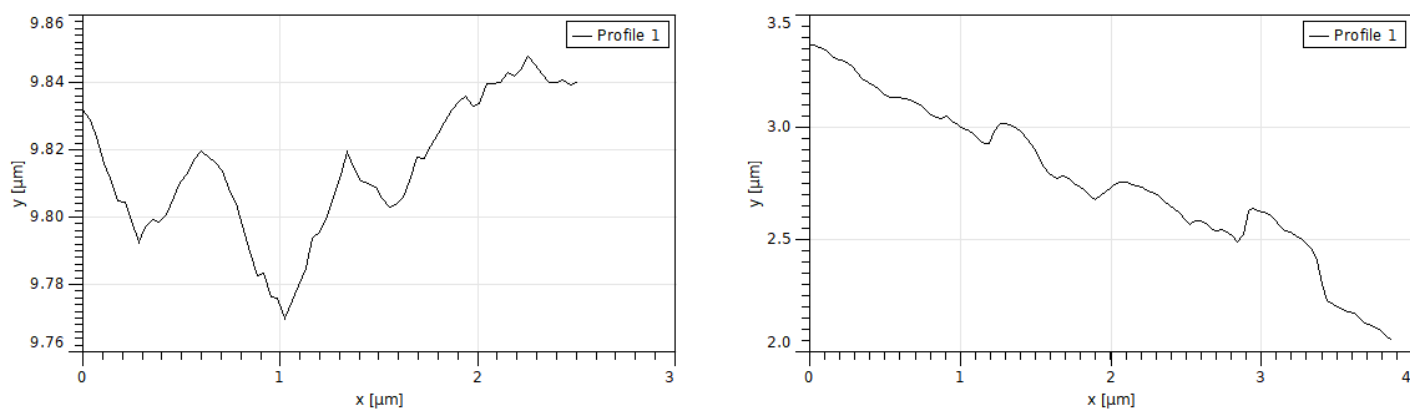


Figure S2. Profiles taken across the black boxes in the above images show surface features consistent with the roughness statistics from S1.



Figure S3. Neat 3MOT reacted with HKUST-1 directly yields a coating of polymer on the crystal surface visible in SEM. Unlike the EDOT composite, the P3MOT film is compact and fine-pored.

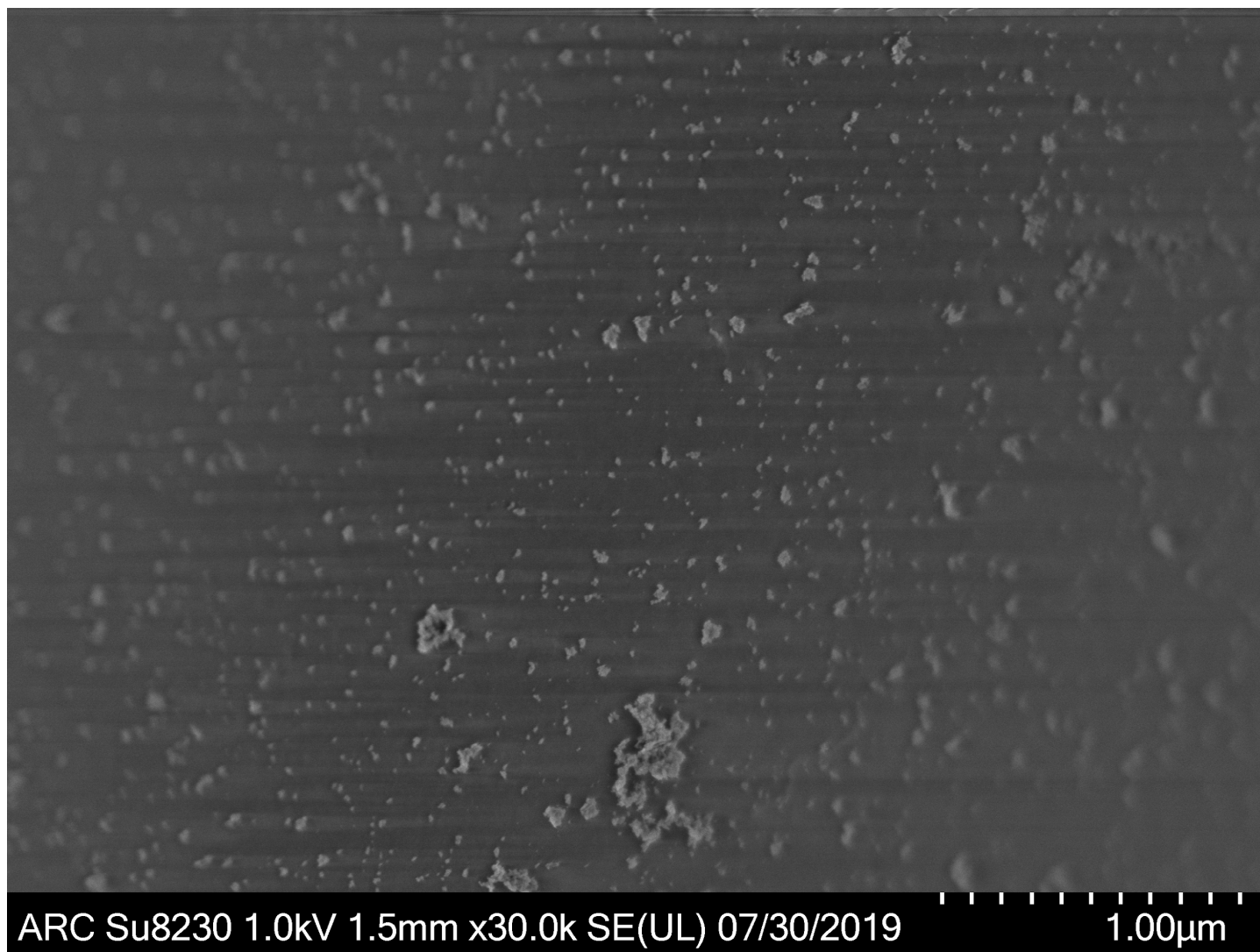


Figure S4. Neat 3HOT gives only irregular flakes of polymer on the surface of a HKUST-1 crystal, due to the greater solubility of P3HOT.



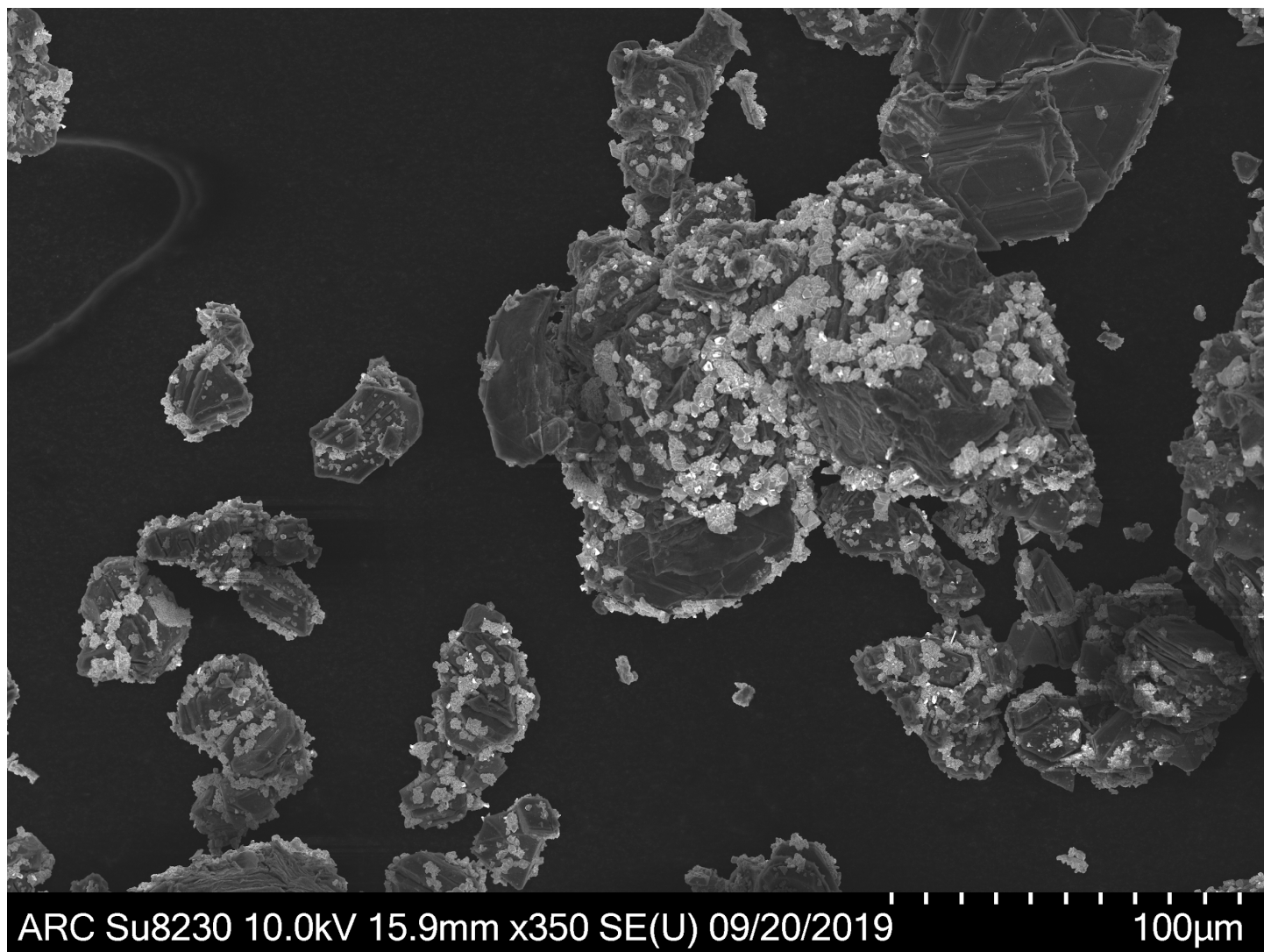


Figure S5. Attempts to prepare HKUST/PEDOT composites by iodine polymerization of hexane-loaded MOF resulted in the near-complete destruction of the crystalline lattice.



Figure S6. 3MOT loaded in hexanes and heated does not show polymer nodules or coating on the HKUST-1 surface.

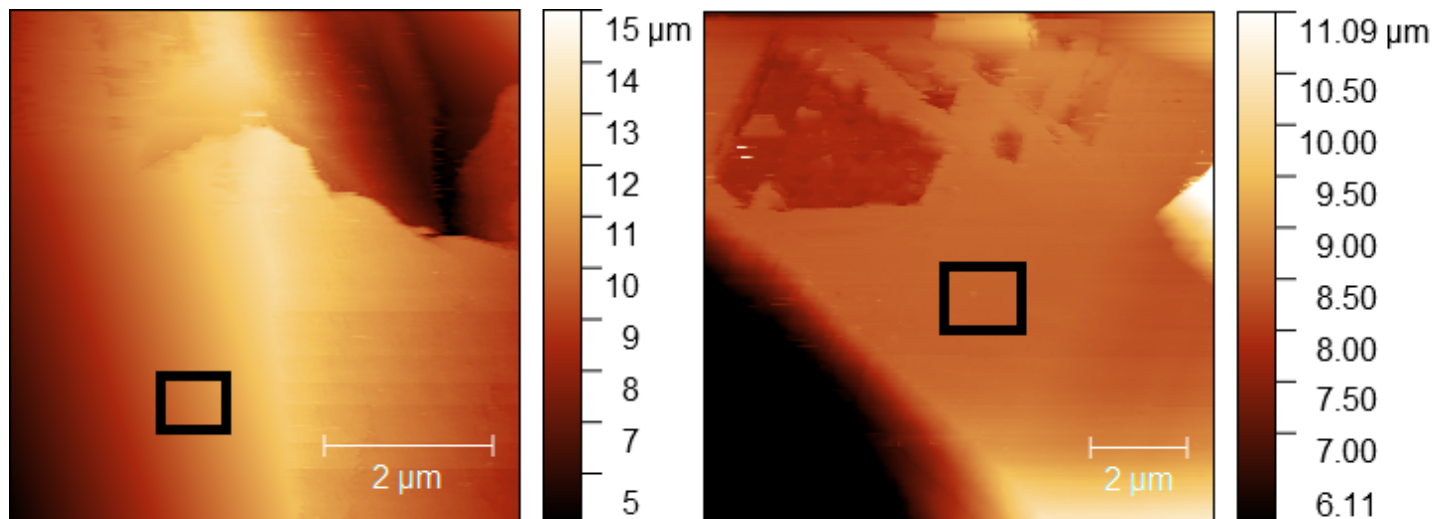


Figure S7. Both hexane-loaded (left, 22 nm RMS roughness) and neat (right) 3MOT/HKUST-1 composite show smooth surfaces by AFM, consistent with the more compact P3MOT film seen in SEM imaging (Figure S3)

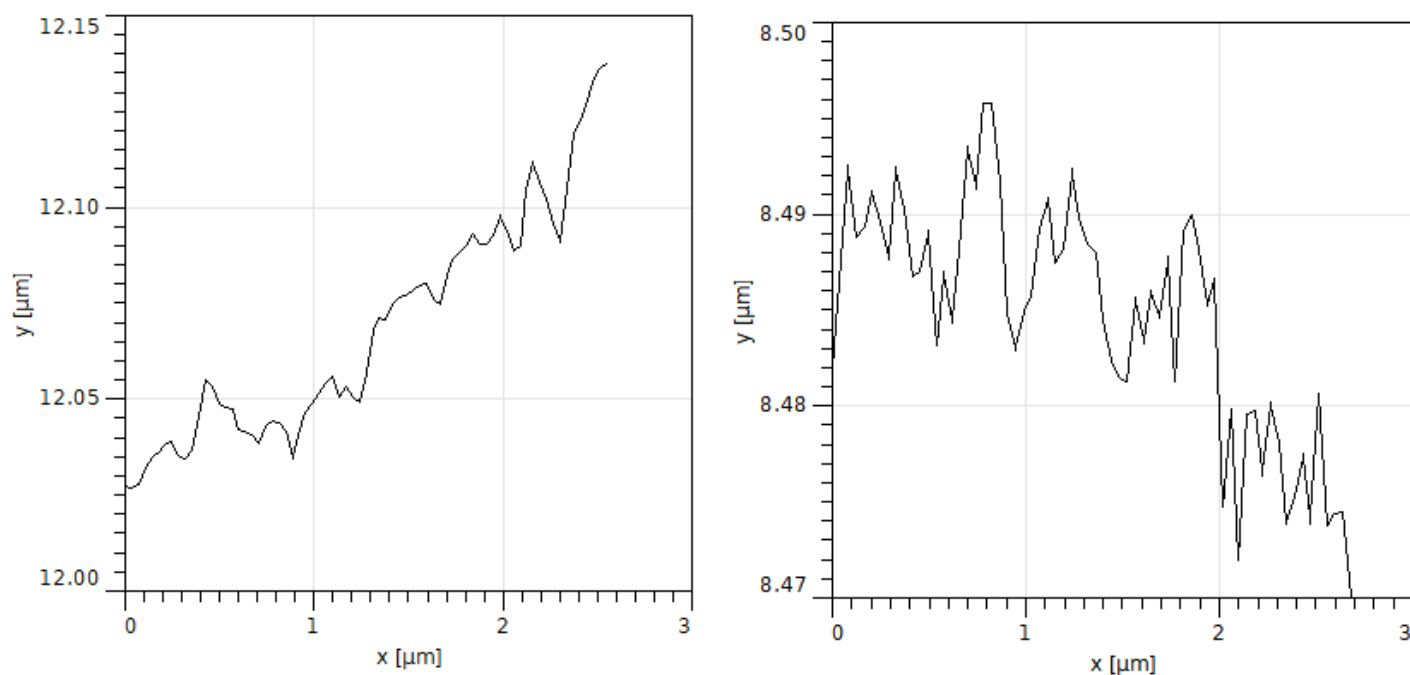


Figure S8. Line profiles taken across the black boxes shown in both AFM images (Fig. S7) demonstrate surface features of only a few nm on both hexane-loaded (left) and neat (right) 3MOT composites.

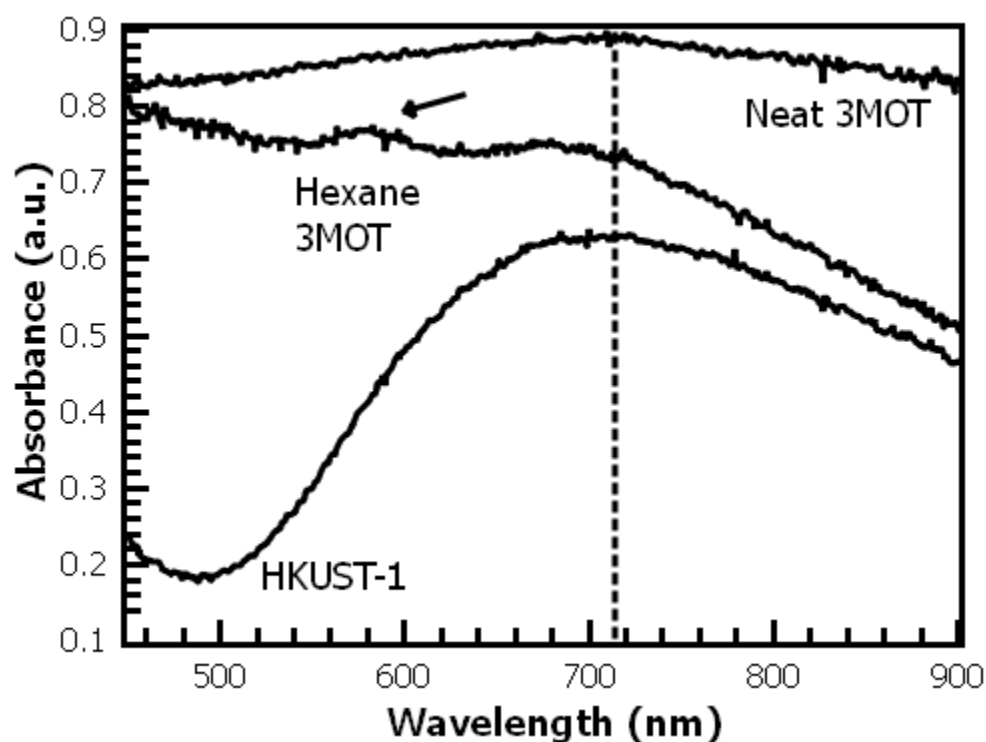
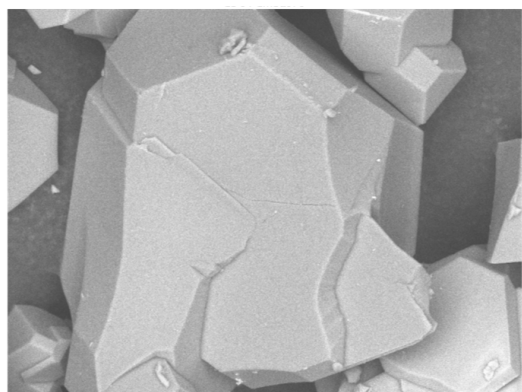
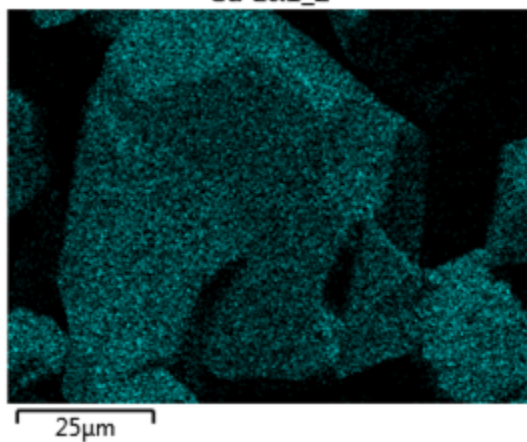


Figure S9. Reflectance absorption spectroscopy of 3MOT composites shows a qualitative difference between the hexane-loaded and neat composites, with the characteristically redshifted LMCT transition of HKUST-1 (arrow) containing a guest material.



Cu L $\alpha$ 1\_2



S K $\alpha$ 1

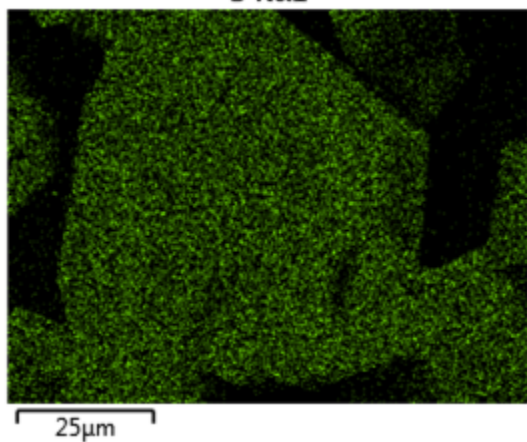
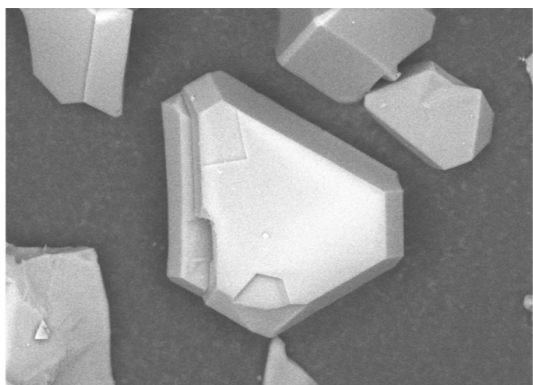
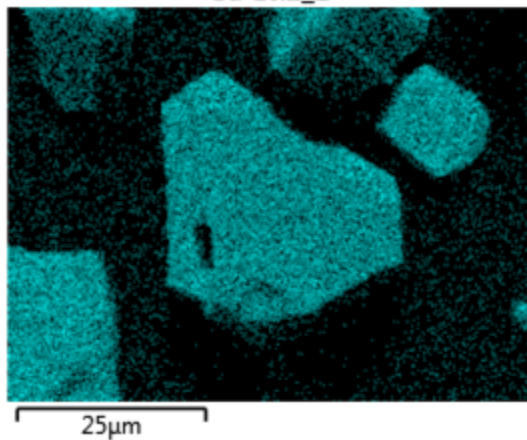


Figure S10. Electron image, Cu La1 line, and sulfur Ka1 line images for neat EDOT.



Cu  $L\alpha_{1,2}$



S  $K\alpha_1$

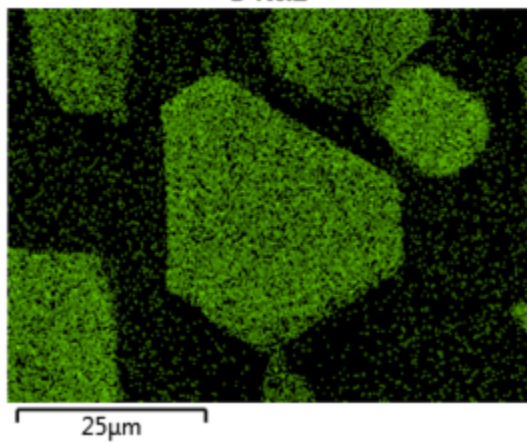
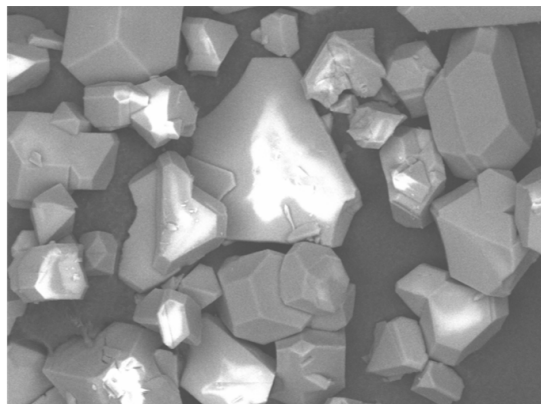
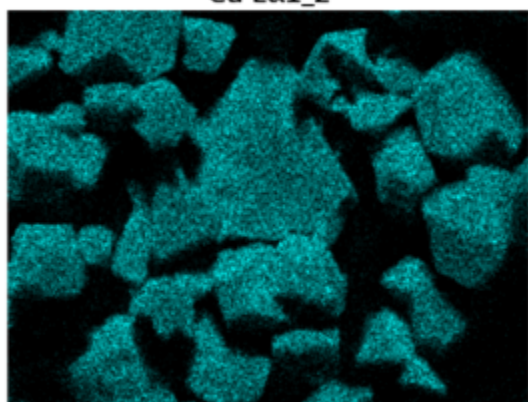


Figure S11. Electron image, Cu  $L\alpha_1$  line, and sulfur  $K\alpha_1$  line images for EDOT loaded in hexanes.





Cu  $L\alpha_{1,2}$



S  $K\alpha_1$

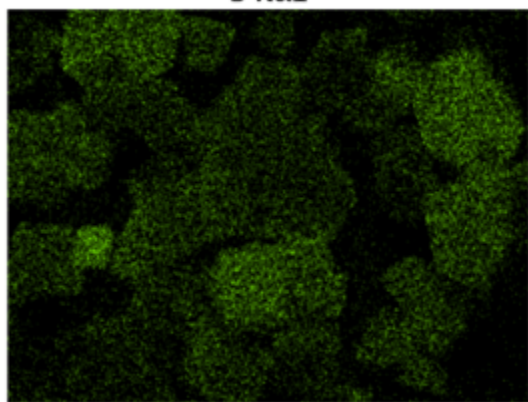
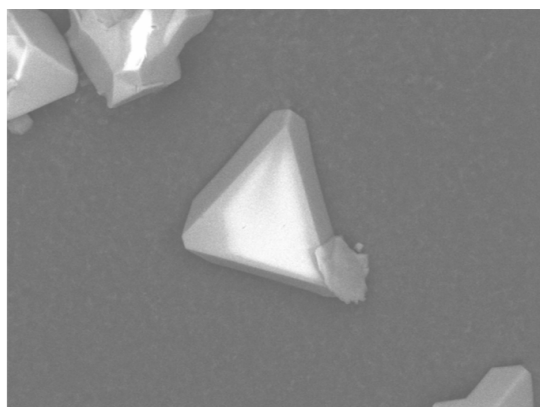
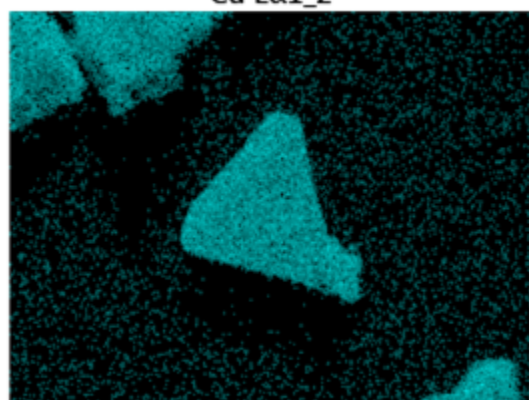


Figure S12. Electron image, Cu  $L\alpha_1$  line, and sulfur  $K\alpha_1$  line images for neat 3MOT.



Cu L $\alpha$ 1\_2



S K $\alpha$ 1

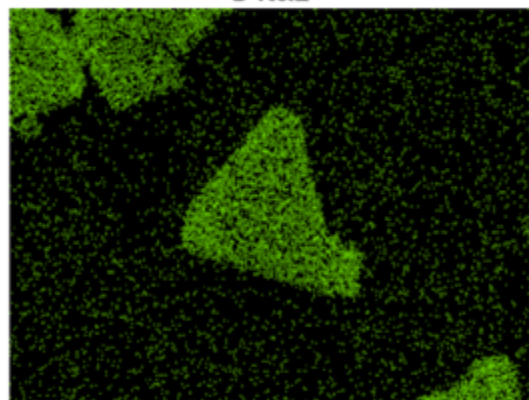
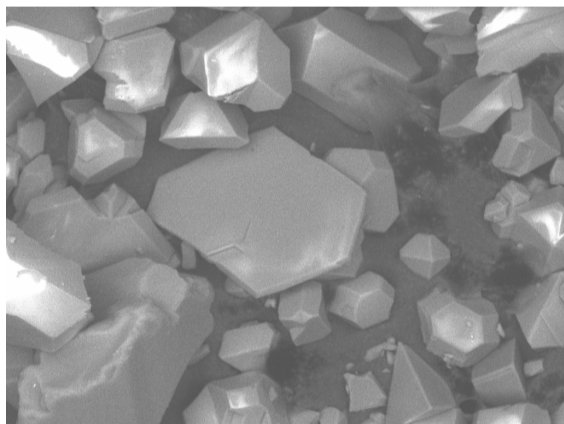
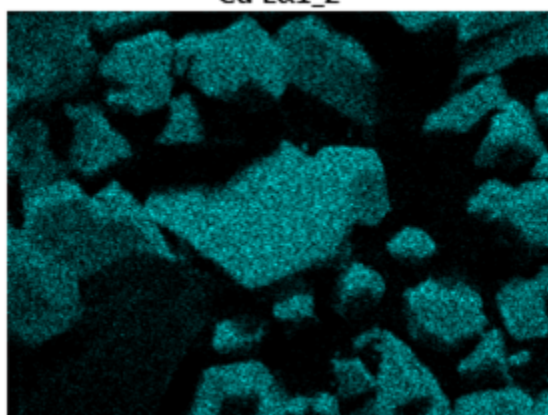


Figure S13. Electron image, Cu La1 line, and sulfur Ka1 line images for 3MOT loaded in hexanes.



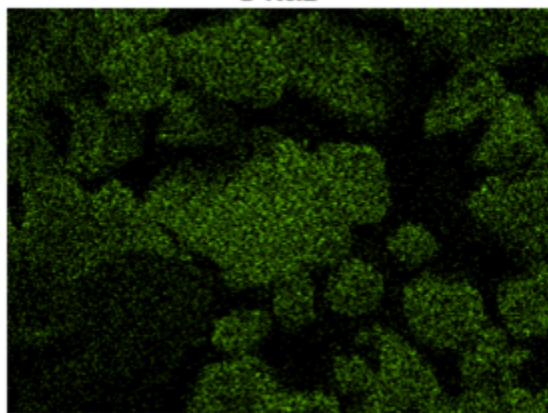


Cu L $\alpha$ 1\_2



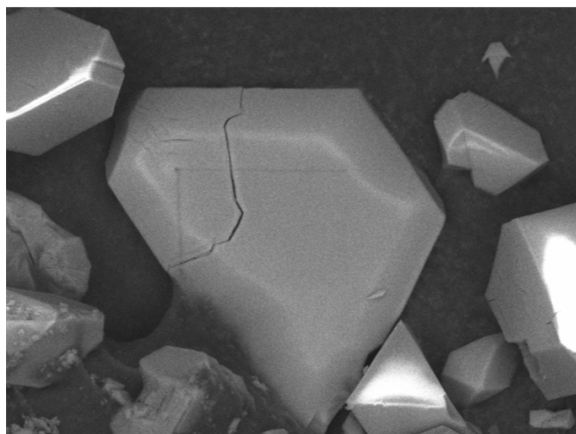
50 $\mu$ m

S K $\alpha$ 1

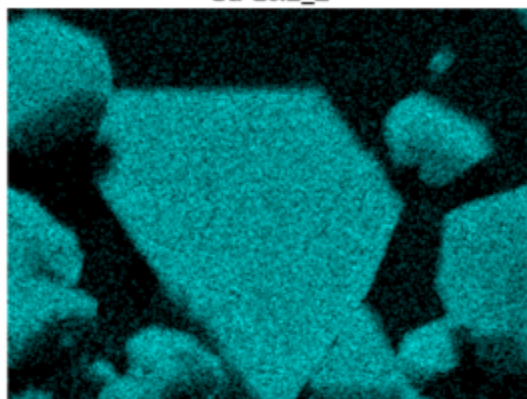


50 $\mu$ m

Figure S14. Electron image, Cu La1 line, and sulfur Ka1 line images for neat 3HOT.



Cu L $\alpha$ 1\_2



S K $\alpha$ 1

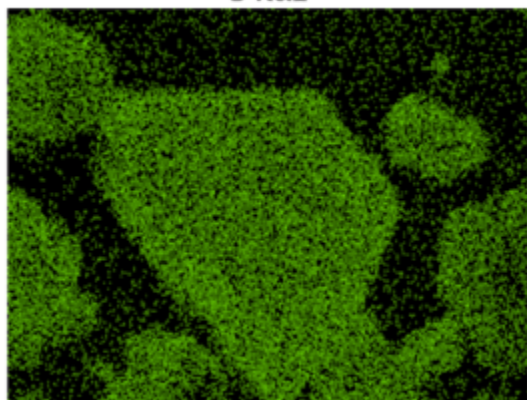


Figure S15. Electron image, Cu La1 line, and sulfur Ka1 line images for 3HOT loaded in hexanes.

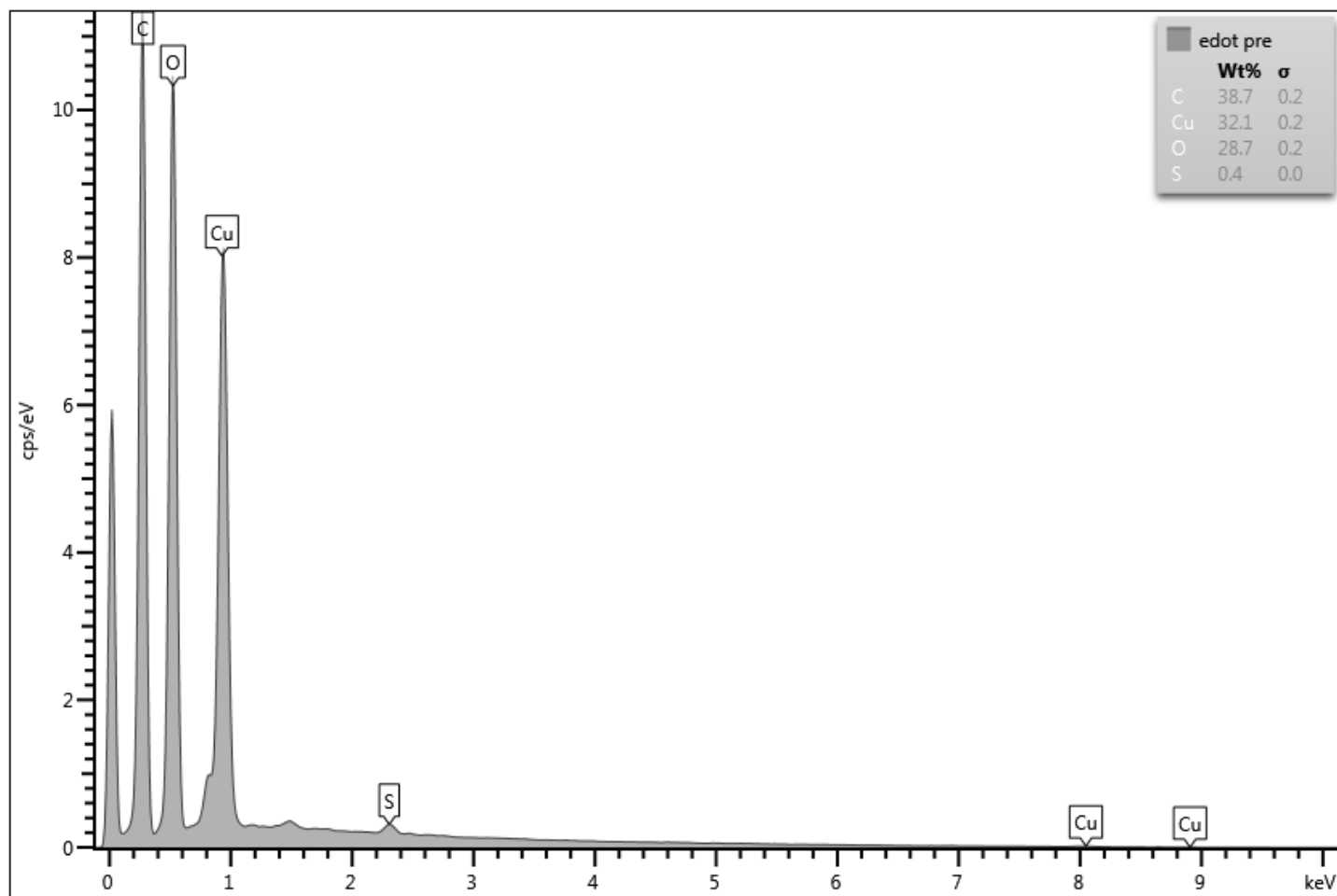


Figure S16. EDS spectrum of EDOT monomer loaded in hexanes into HKUST-1, but not polymerized. Relatively little sulfur is detected.