SUPPLEMENTAL INFORMATION FOR:

Solvent-driven transformation of Zn/Cd^{2+}-deoxycholate assemblies

Rachelle M. S. Smith[1], Mehran Amiri[1], Nicolas P. Martin[1,2], Alice Lulich[1], Lauren N. Palys,[1] Guomin Zhu[3], James J. De Yoreo[3,4] and May Nyman[1*]

[1]Department of Chemistry, Oregon State University, Corvallis, OR 97330 USA
[2]current address: Institut Jean Lamour, UMR 7198 CNRS – Université de Lorraine, Campus ARTEM, 2 allée André Guinier, 54011, Nancy, France
[3]Department of Materials Science and Engineering, University of Washington, Seattle, WA, 98195
[4]Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99354
*corresponding author: may.nyman@oregonstate.edu

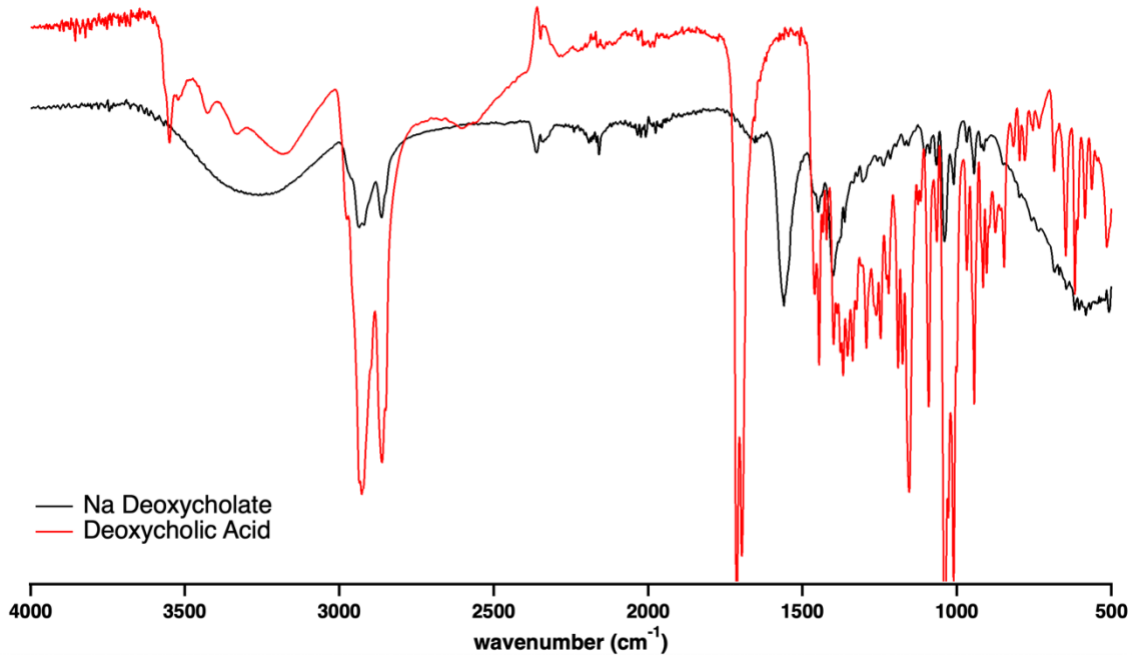

Figure S1. FT-IR of the synthesized sodium deoxycholate (Na-DOC). The formation of the salt is evident by the disappearance of the peaks from ~3600-3450 cm^{-1} which is the bonded OH on the carboxylic acid. The shift of the peak at ~1700 cm^{-1} to 1600cm^{-1}, as well, shows the change from a carboxylic acid to a carboxylate species.

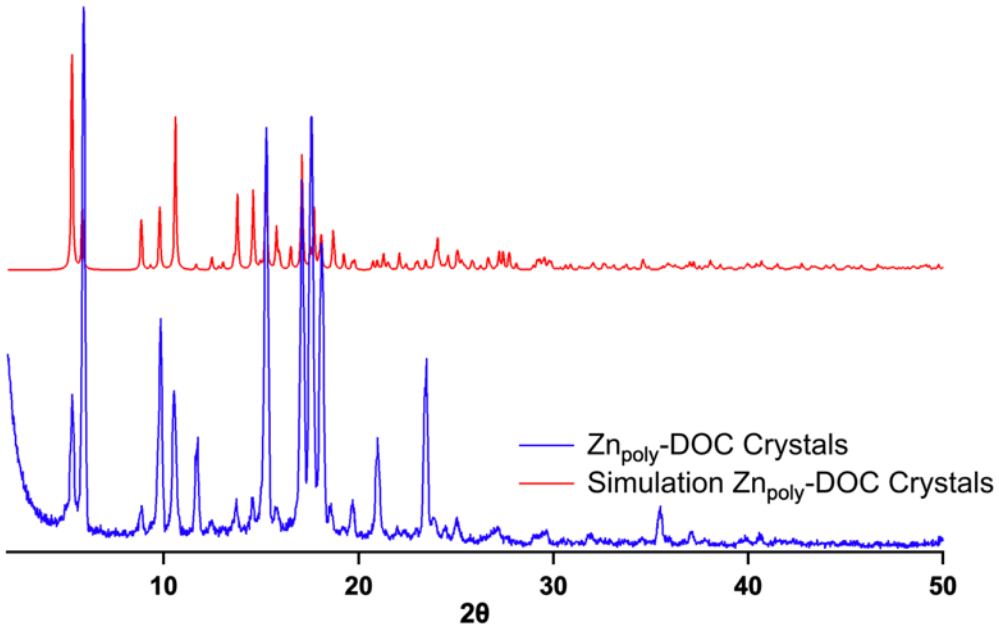

Figure S2. PXRD of **Zn_{poly}-DOC** shows the bulk purity of the crystals. They show clear preferential orientation.

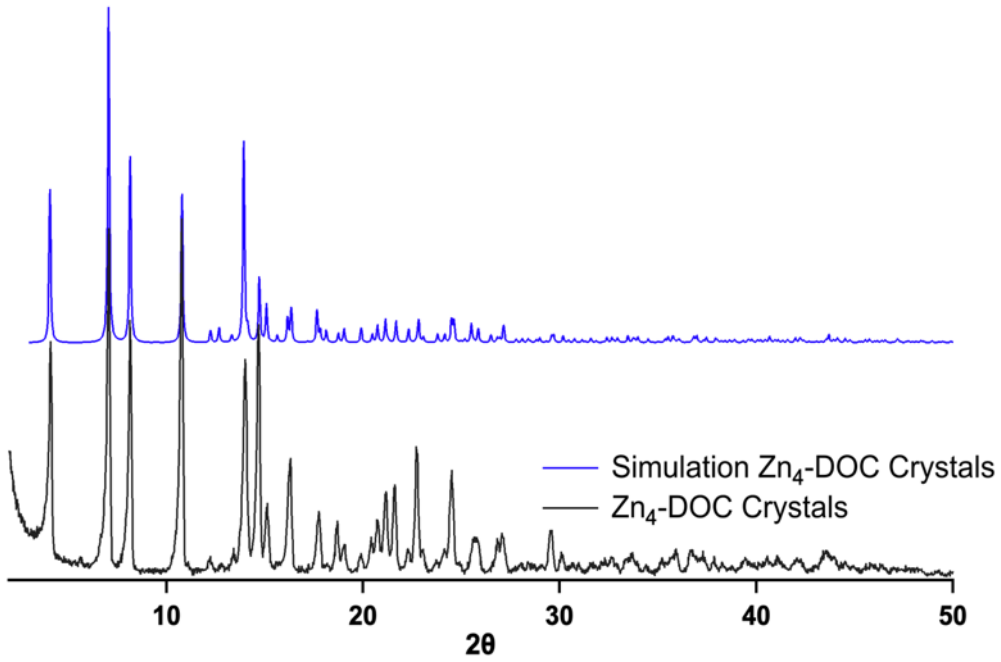

Figure S3. Zn_4-DOC bulk purity shown by PXRD.

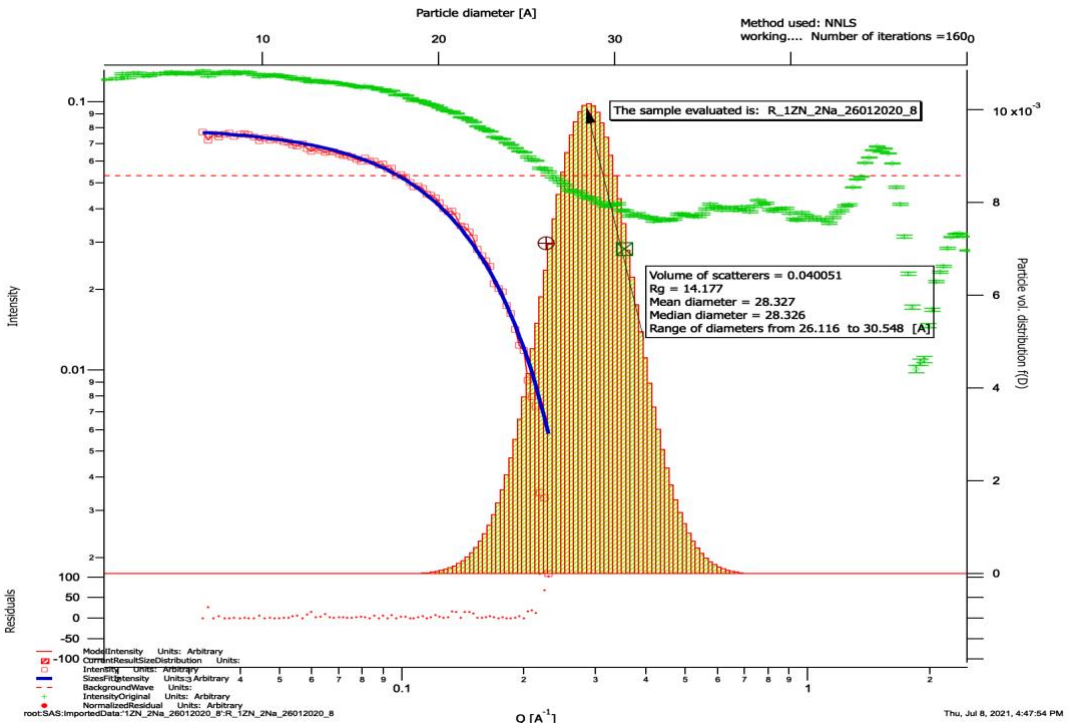

Figure S4. Size distribution of the **Zn_{poly}-DOC** bulk precipitate dissolved in MeOH. Green curve is the original scattering curve, red curve is the original curve minus a flat background, background is the red dashed horizontal line. Blue line is the model of the fit as a spherical particle. Red and green bar graph is the results of the size distribution analysis (also shown in **figure 4B**).

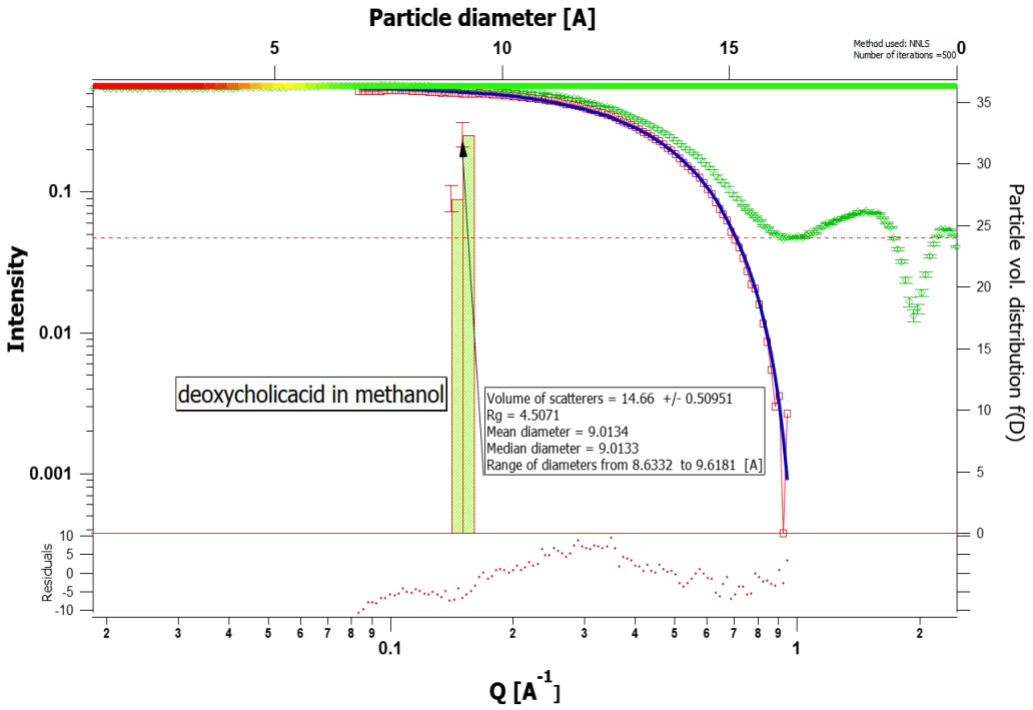

Figure S5. Size distribution of deoxycholic acid in methanol shows an extremely narrow shape indicating that it is a more spherical shape. We see a diameter of 9Å which indicates one individual deoxycholate in solution as opposed to a dimer or larger aggregates.

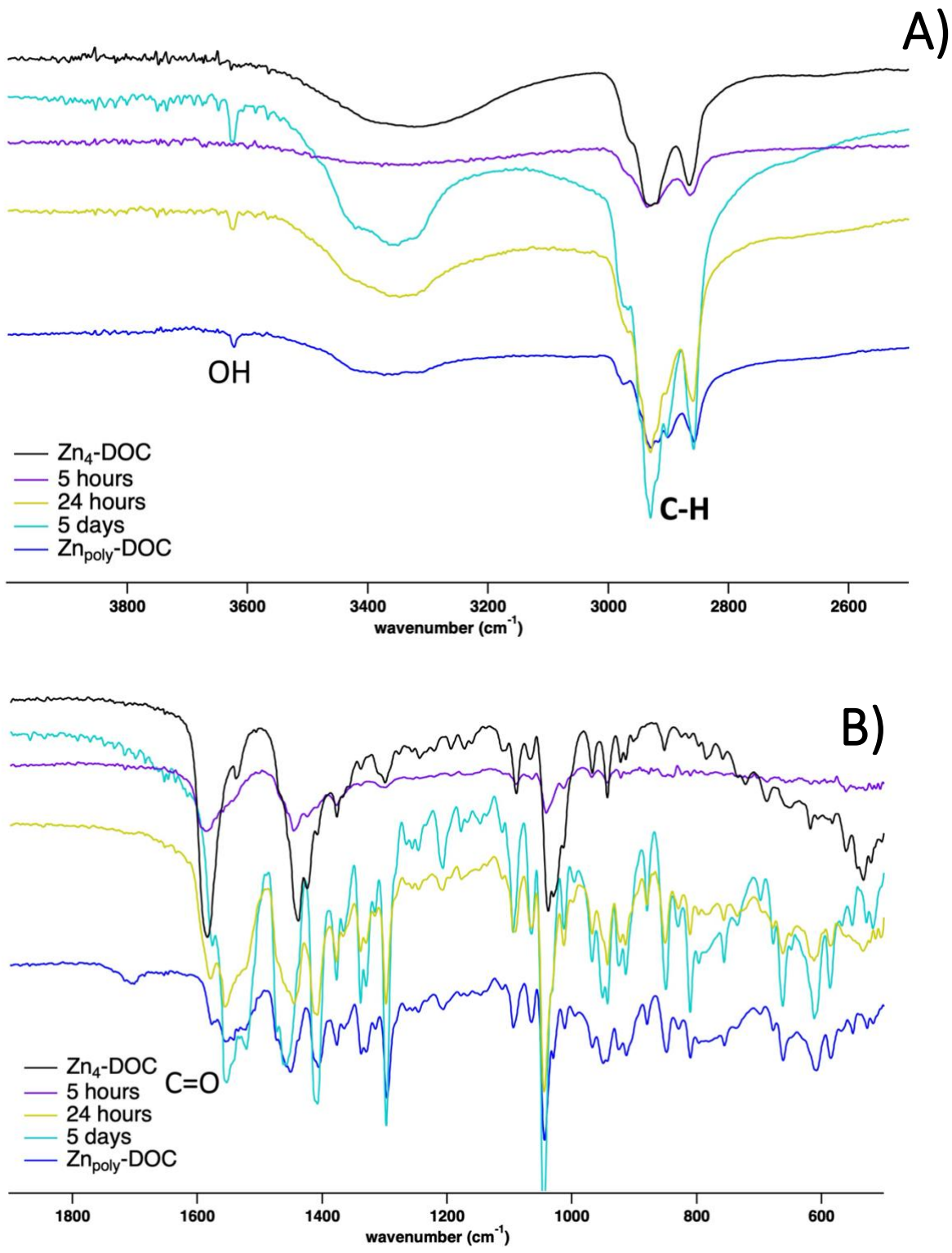

Figure S6. FT-IR shows the transformation from **Zn_4-DOC** to **Zn_{poly}-DOC** upon soaking in water. Key features are highlighted: **A)** shows the growth of a sharp and small peak at ~3600 cm^{-1}. This is the water bonded to the Zn in the **Zn_{poly}-DOC**. Here it increases until 5 days. **B)** shows the more complex fingerprint regions. Focusing on the carboxylate bands at ~1600 cm^{-1}, **Zn_4-DOC** has one strong band, since all the deoxycholate ligands bridge the zinc-centers in the same way. The carboxylates of **Zn_{poly}-DOC** bonding is both monodentate and bidentate, yielding a split peak.

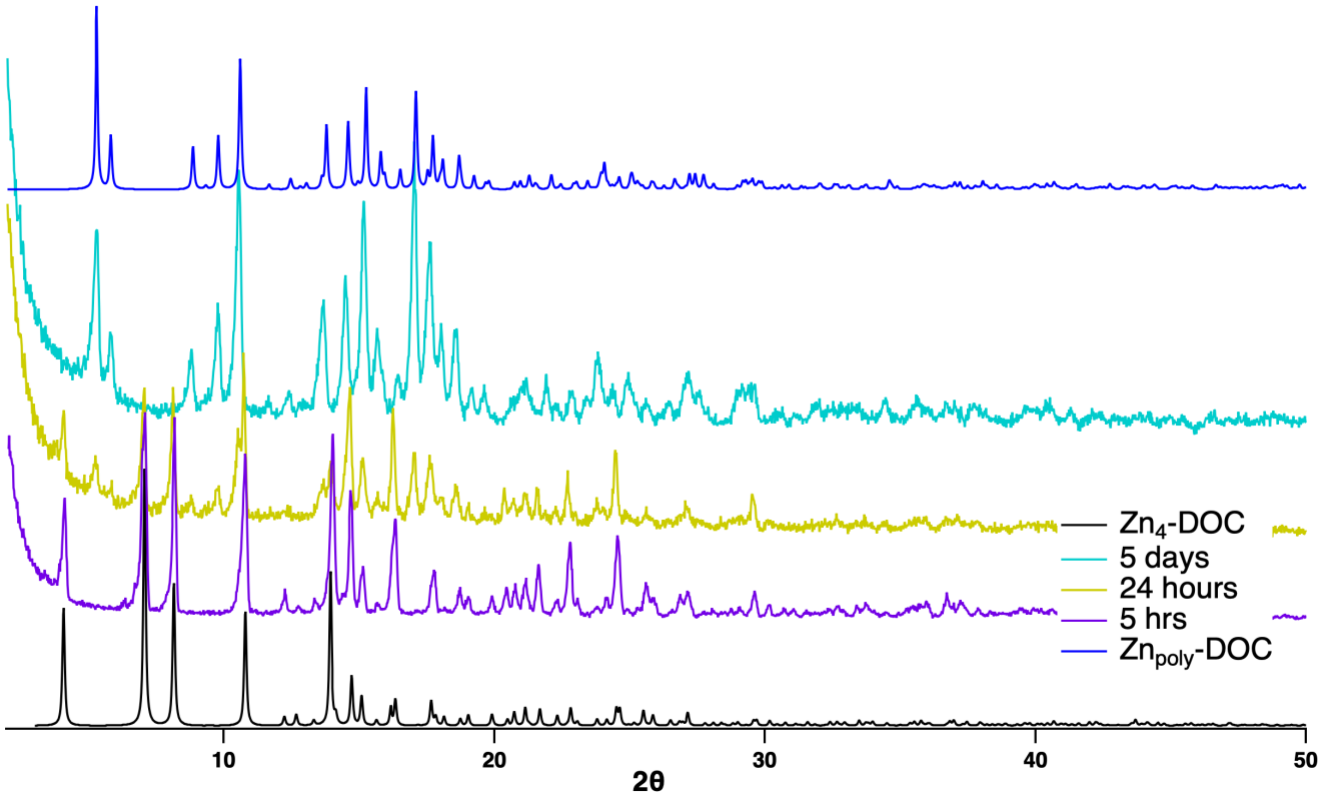

Figure S7. PXRD change shows the transformation from **Zn_4-DOC** to **Zn_{poly}-DOC**. The black and blue spectra are simulated from single-crystal X-ray data, and the green, purple, green and turquoise are experimental.

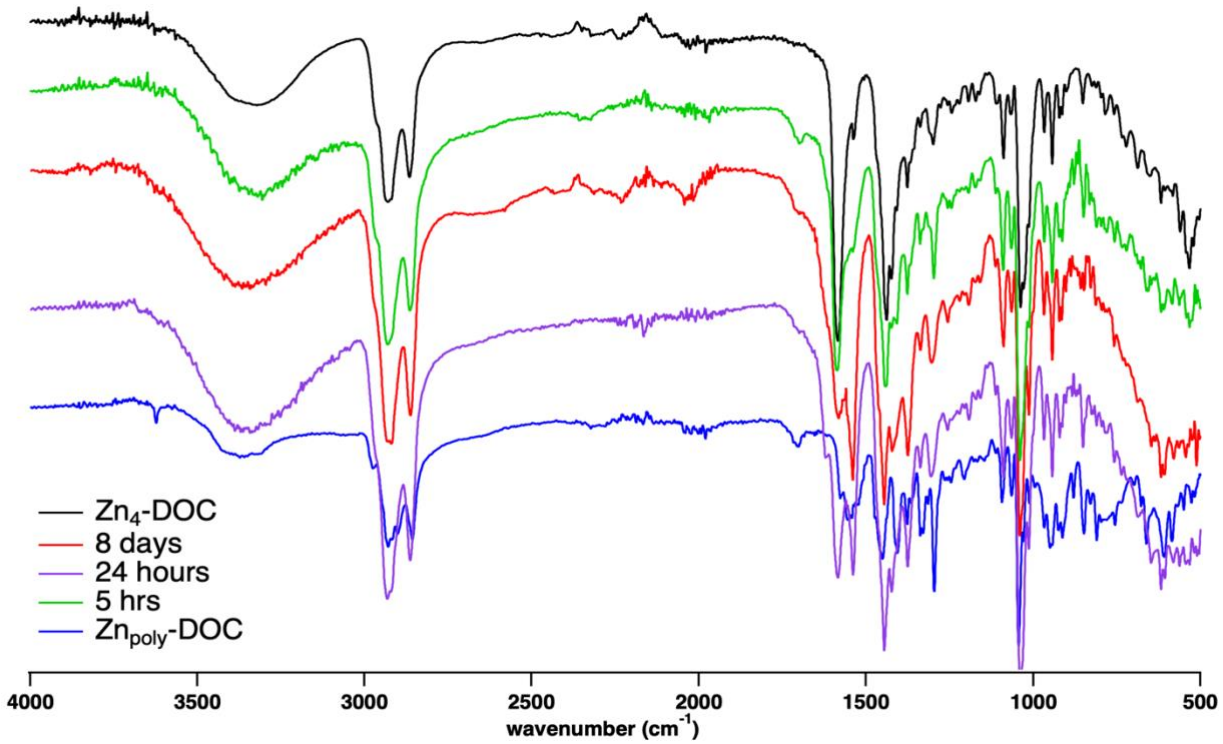

Figure S8. FT-IR shows the transformation of **Zn_{poly}-DOC** to **Zn_4-DOC** that results from MeOH diffusion. After 5 hours (green), we observe a match with pristine **Zn_4-DOC** (black). The peak at 3600 cm^{-1} which is one of the key characteristics of the **Zn_{poly}-DOC** disappeared.

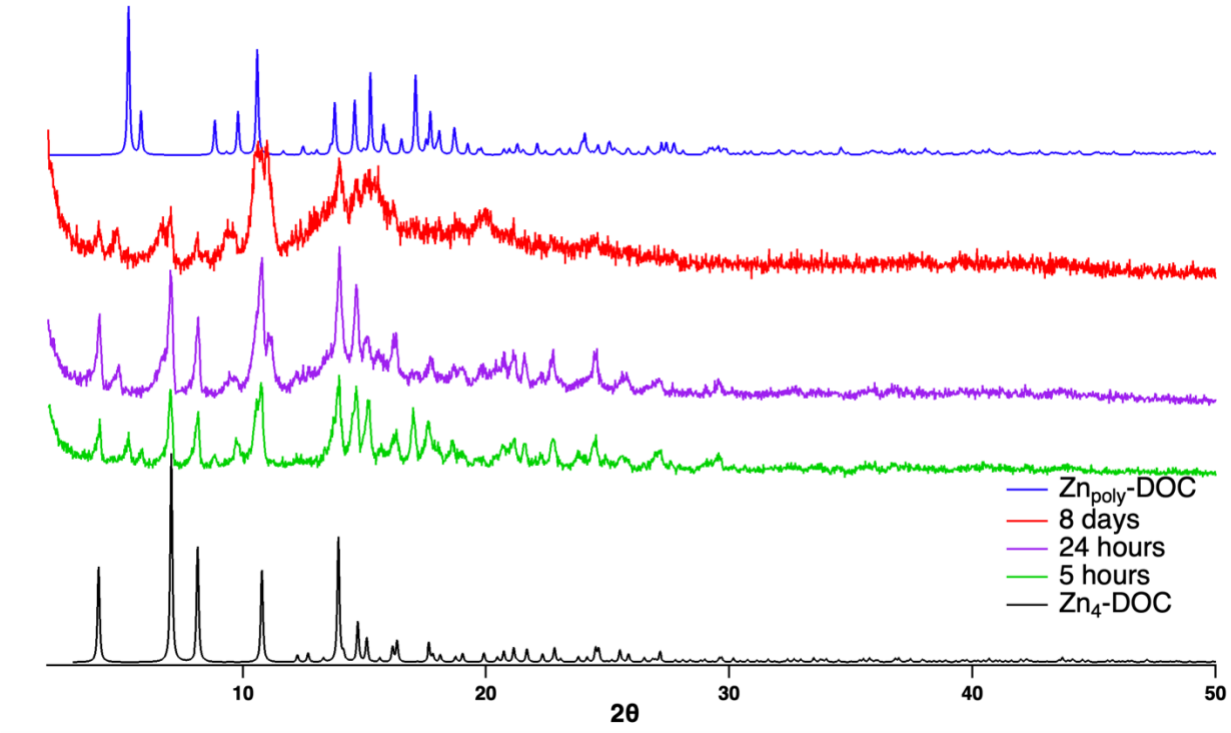

Figure S9. PXRD of the MeOH diffusion of **Zn_{poly}-DOC**, showing loss of long-range order. The black and blue spectra are simulated from single-crystal X-ray data, and the green, purple and red are experimental.

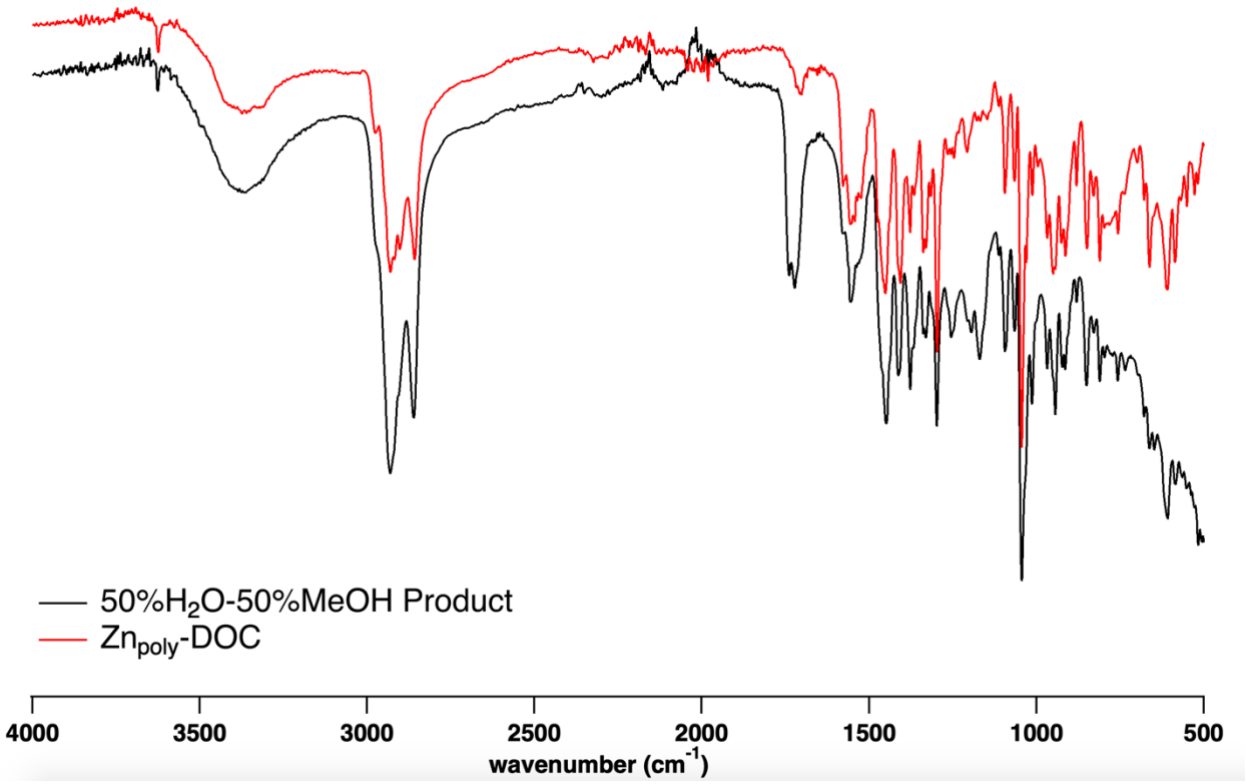

Figure S10. Synthesis in mixed solvent shows the preferential structure is the **Zn_{poly}-DOC** polymeric structure. We do see a peak at 1700 cm^{-1} which indicates that some of the deoxycholate is protonated.

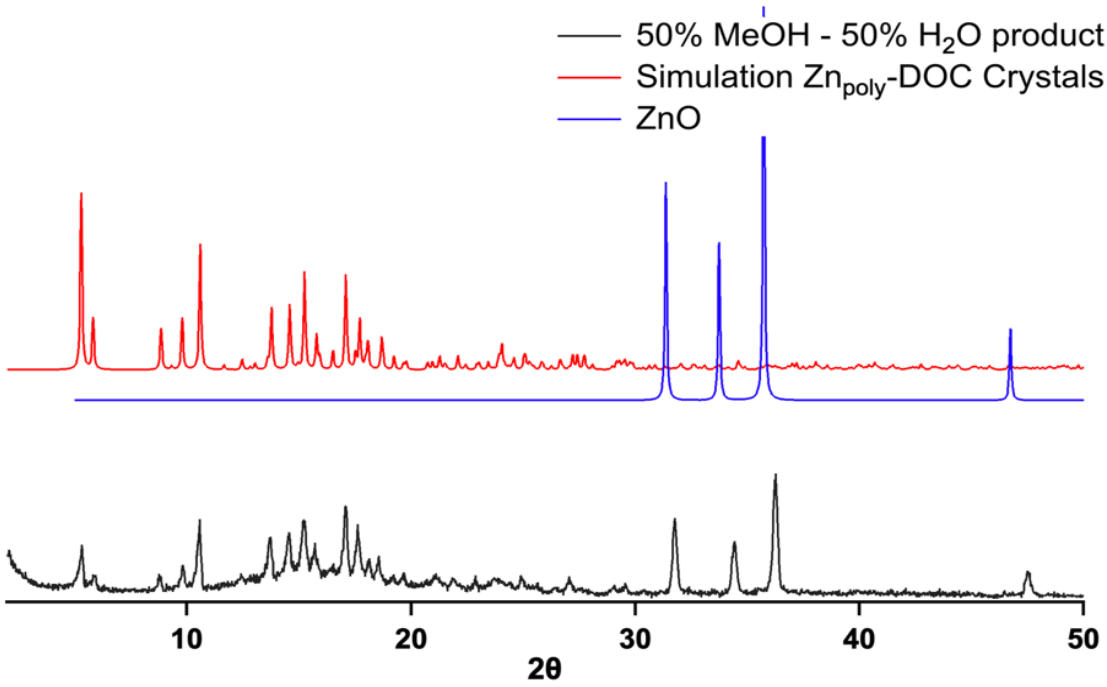

Figure S11. PXRD of mixed solvent shows that the product matches **Zn_{poly}-DOC** with some ZnO byproduct. The blue and red spectra are simulated from single-crystal X-ray data, and the black is experimental.

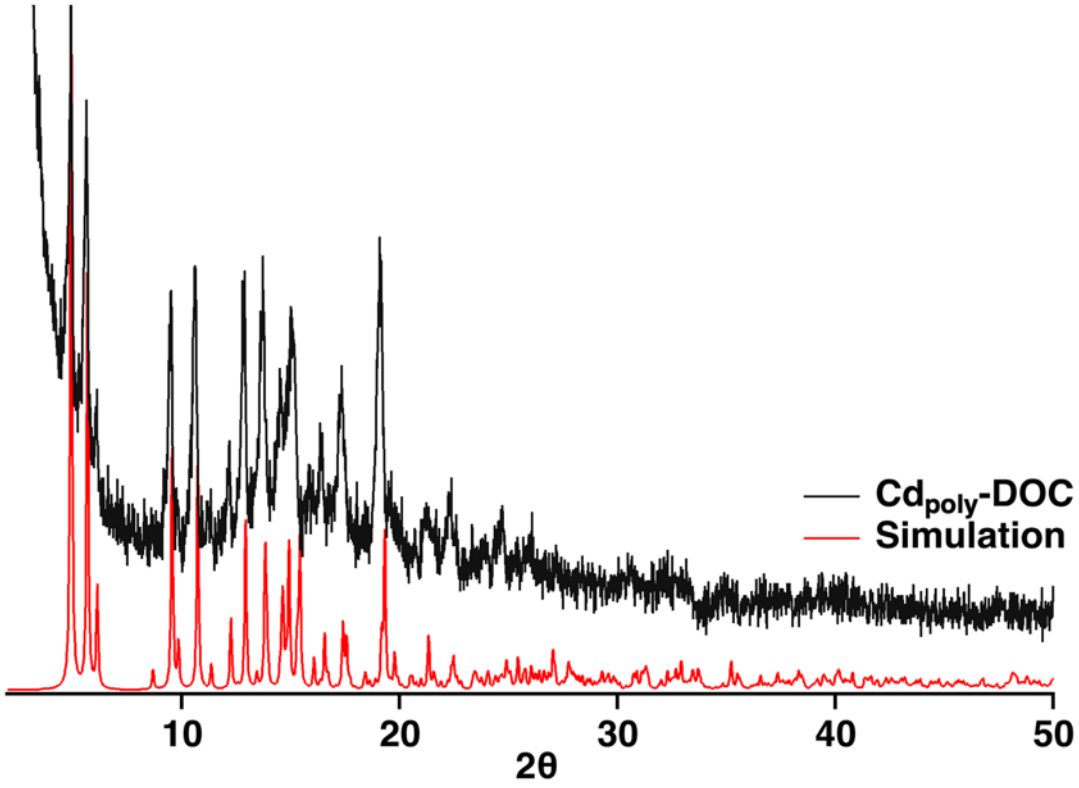

Figure S12. PXRD of **Cd$_{poly}$-DOC** shows a match with the PXRD simulated from the single-crystal structure.

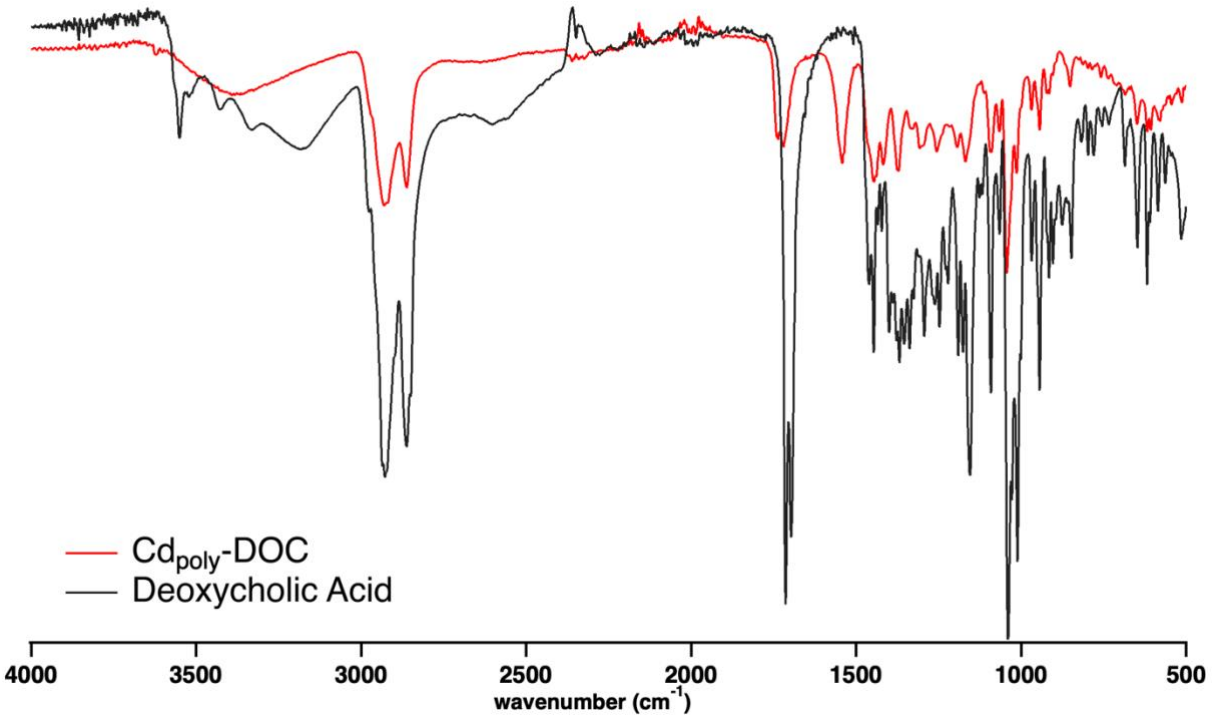

Figure S13. FT-IR of **Cd$_{poly}$-DOC** crystals compared to that of deoxycholic acid.

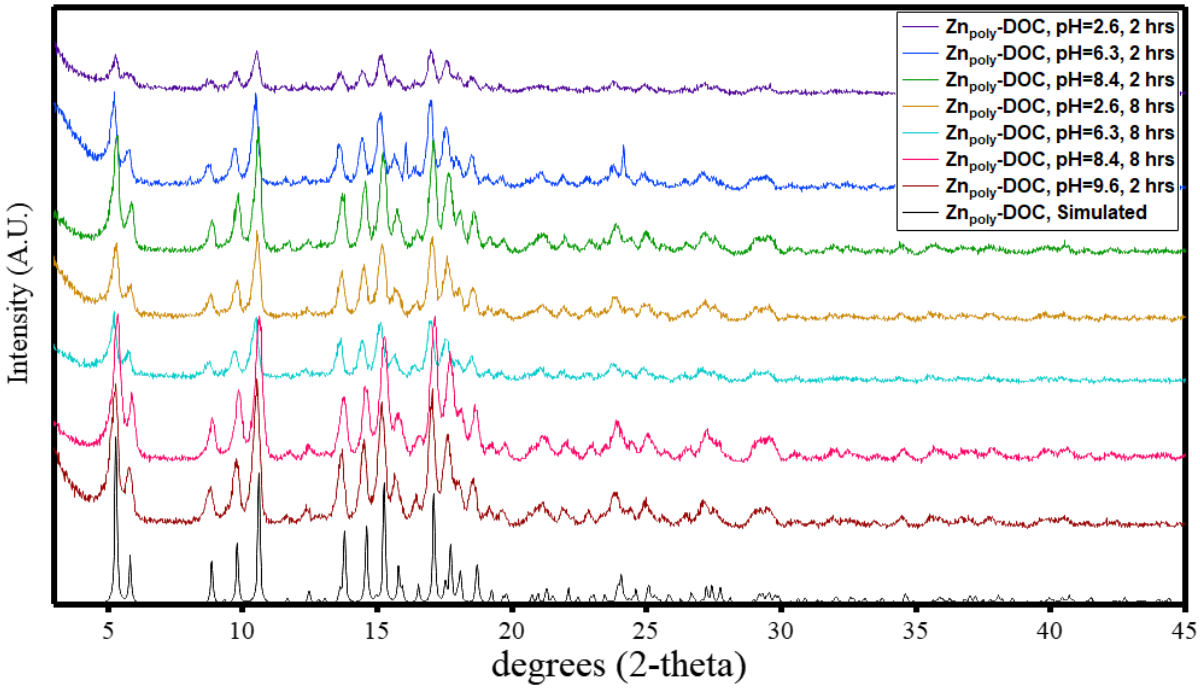

Figure S14. PXRD of **Zn$_{poly}$-DOC** pH-stability tests, showing stability between pH ~ 6 to 9.

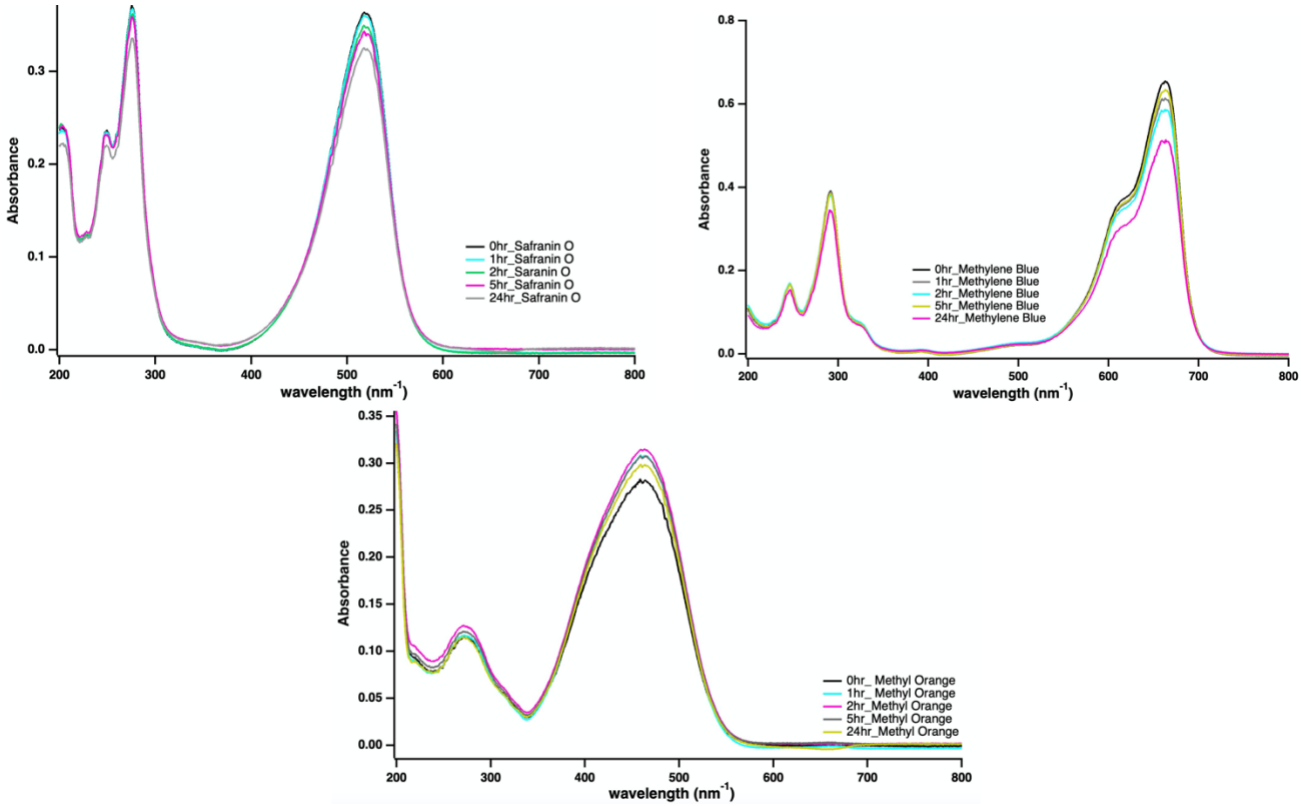

Figure S15. Control experiments of Safranin O and Methylene Blue left in ambient conditions for 24 hours.

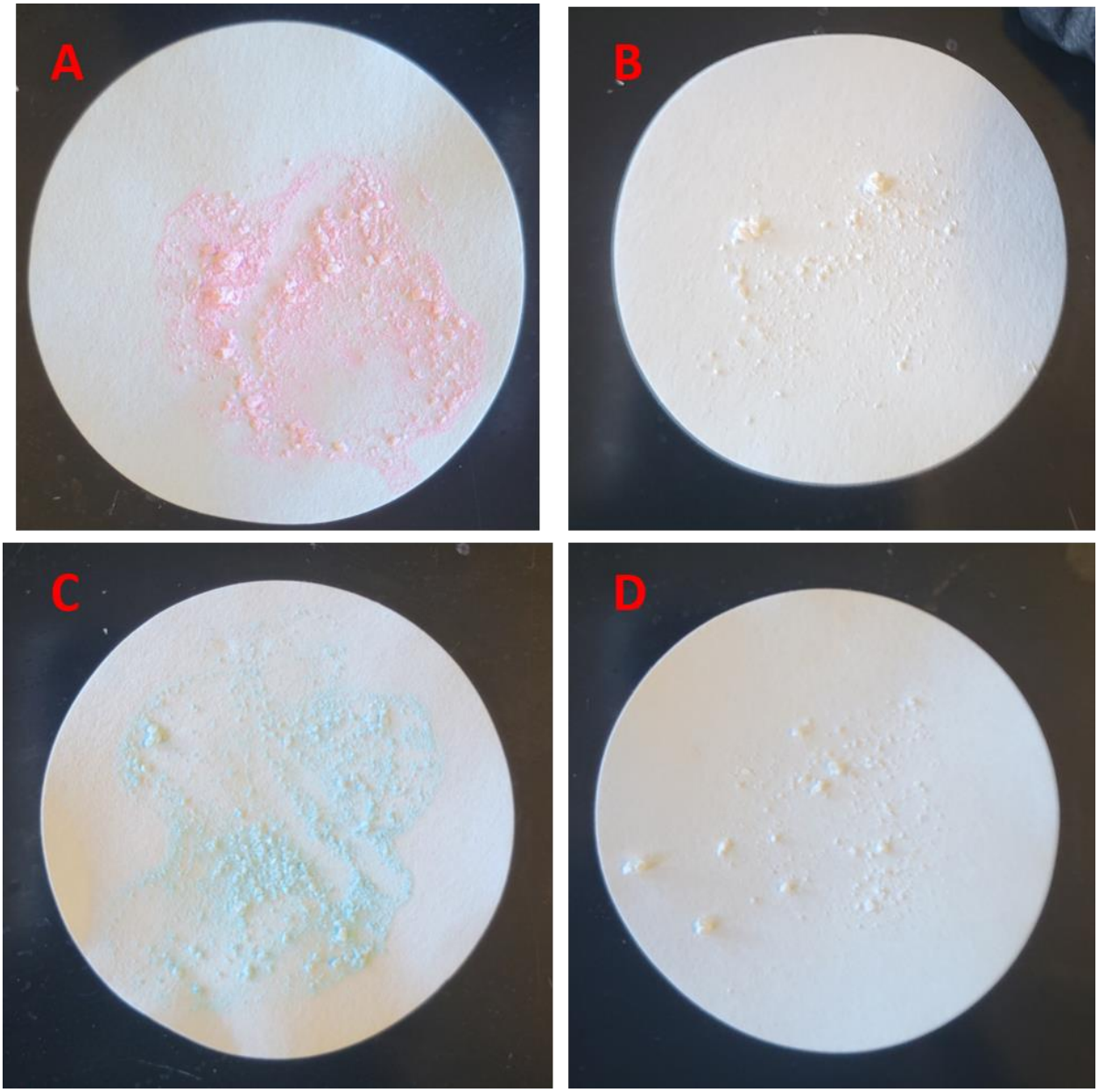

Figure S16. Visual demonstration of back-extraction of SO and MB with ethanol. **A)** **Zn_{poly}-DOC** with adsorbed SO displaying pink color. **B)** **Zn_{poly}-DOC** after back-extraction of SO with ethanol. **C)** **Zn_{poly}-DOC** with adsorbed MB displaying blue color. **D)** **Zn_{poly}-DOC** after back-extraction of MB with ethanol.

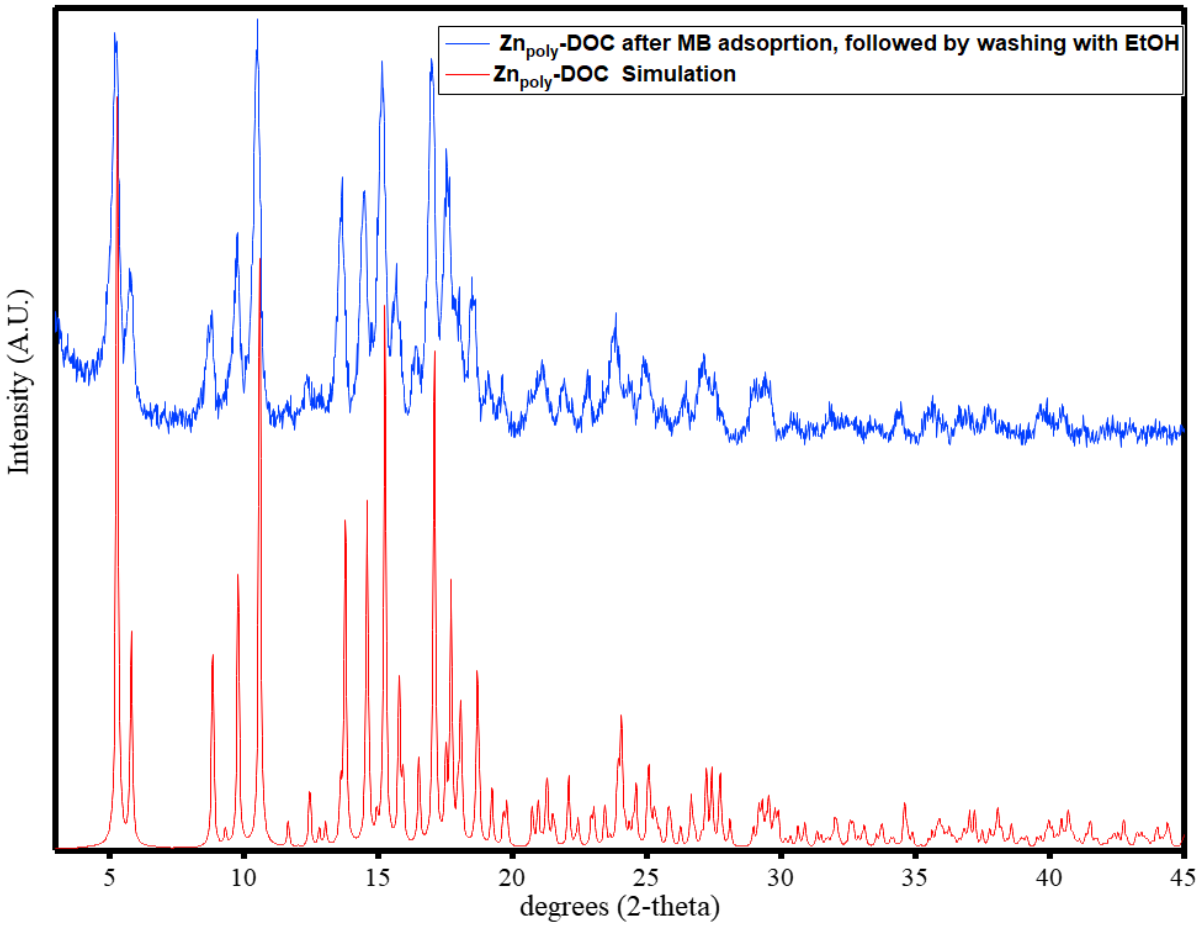

Figure S17. PXRD of **Zn$_{poly}$-DOC** after adsorption of MB (methylene blue), followed by washing with ethanol, demonstrating that, unlike methanol, the ethanol wash does not change the polymeric structure.