Supplementary Information (SI)

Microwave synthesis of upconverting nanoparticles with bis(2-ethylhexyl) adipate

Ana Egatz-Gomez,[*a,b] Michaela Asher,[a,b] Rozabel Peterson,[a,b] Manuel A. Roldan,[c] and Alexandra Ros[a,b]

[a] School of Molecular Sciences, Arizona State University, Tempe, Arizona, USA
[b] Center for Applied Structural Discovery, Biodesign Institute, Arizona State University, Tempe, Arizona, USA
[c] John M. Cowley Center for High-Resolution Electron Microscopy, Arizona State University, Tempe, Arizona, USA
* Corresponding author: angomez@asu.edu

Preliminary Methods

Preliminary method 1. Trifluoroacetate (TFA) and acetates (Ac) in the stoichiometric proportions for NaY0.802Yb0.18Er0.018F4 (71.20 mg YTFA, 18.77 mg YbTFA, 1.86 mg ErTFA, 35.00 mg NaTFA), 22.5 ml of oleic acid (OA), and 7.50 m of di-n-butyl-phthalate (DBP) were added to a round bottom flask. The reaction was first heated and maintained at 110°C for 10 minutes to dissolve the precursors under magnetic stirring and a gentle Ar flow. The reactor was set to a 300 W fixed power to heat the reaction to 300°C and maintained at a constant 300°C temperature for 10 minutes to induce nanoparticle nucleation and growth (Figure 4A)

Preliminary method 2. Forty-five milliliters of oleic acid (OA), and 15 ml of bis(2-ethylhexyl) adipate (BEHA) were degassed under vacuum and stirred for at least 30 minutes in a round bottom flask. Trifluoroacetate (TFA) and acetates (Ac) in the stoichiometric proportions for $NaY_{0.802}Yb_{0.18}Er_{0.018}F_4$ (463.8 mg YTFA , 91.2 mg YbAc, 9.0 mg ErAc , 123.1 mg NaTFA , 75.1 mg NaAc) were then added to the flask. The flask was placed in the microwave reactor (see Figure 1 for a reactor setup schematic) under stirring and a gentle Ar flow for 30 minutes, then heated to 110°C for 10 minutes to dissolve the precursors, and finally rapidly cooled down to room temperature using compressed air. The solution was split into three aliquots (each with 20 mM rare earth concentration; 33.3 % v/v BEHA, 20 ml reaction volume), and immediately, the aliquots were consecutively run in the microwave reactor. The reactor was set to a 300 W fixed power to heat the reaction to 300°C and maintained at a constant 300°C temperature for 15 minutes to induce nanoparticle nucleation and growth (Figure 4 B-C).

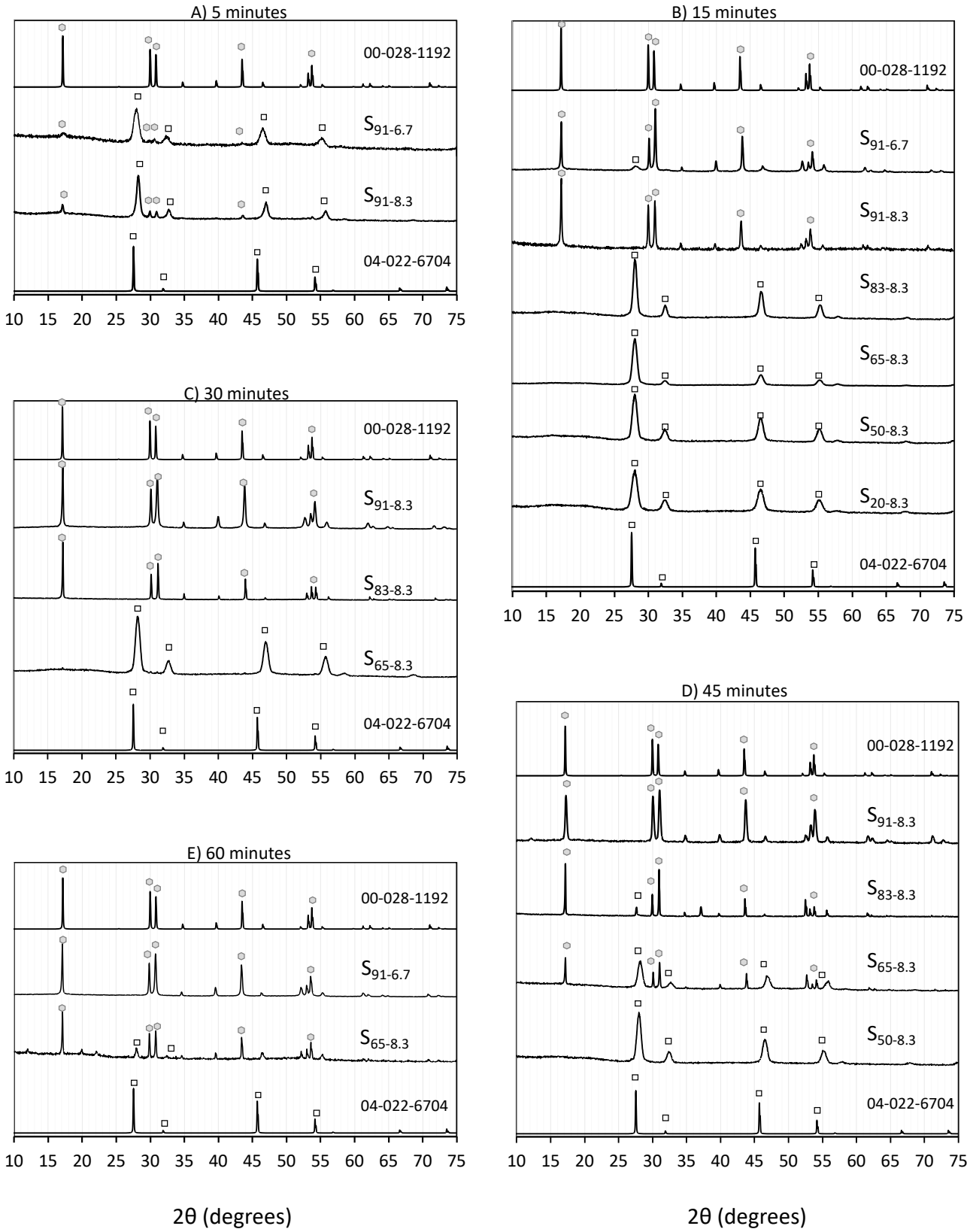

Figure S1. UCNP X-ray diffraction patterns for the complete set of investigated synthesis conditions.

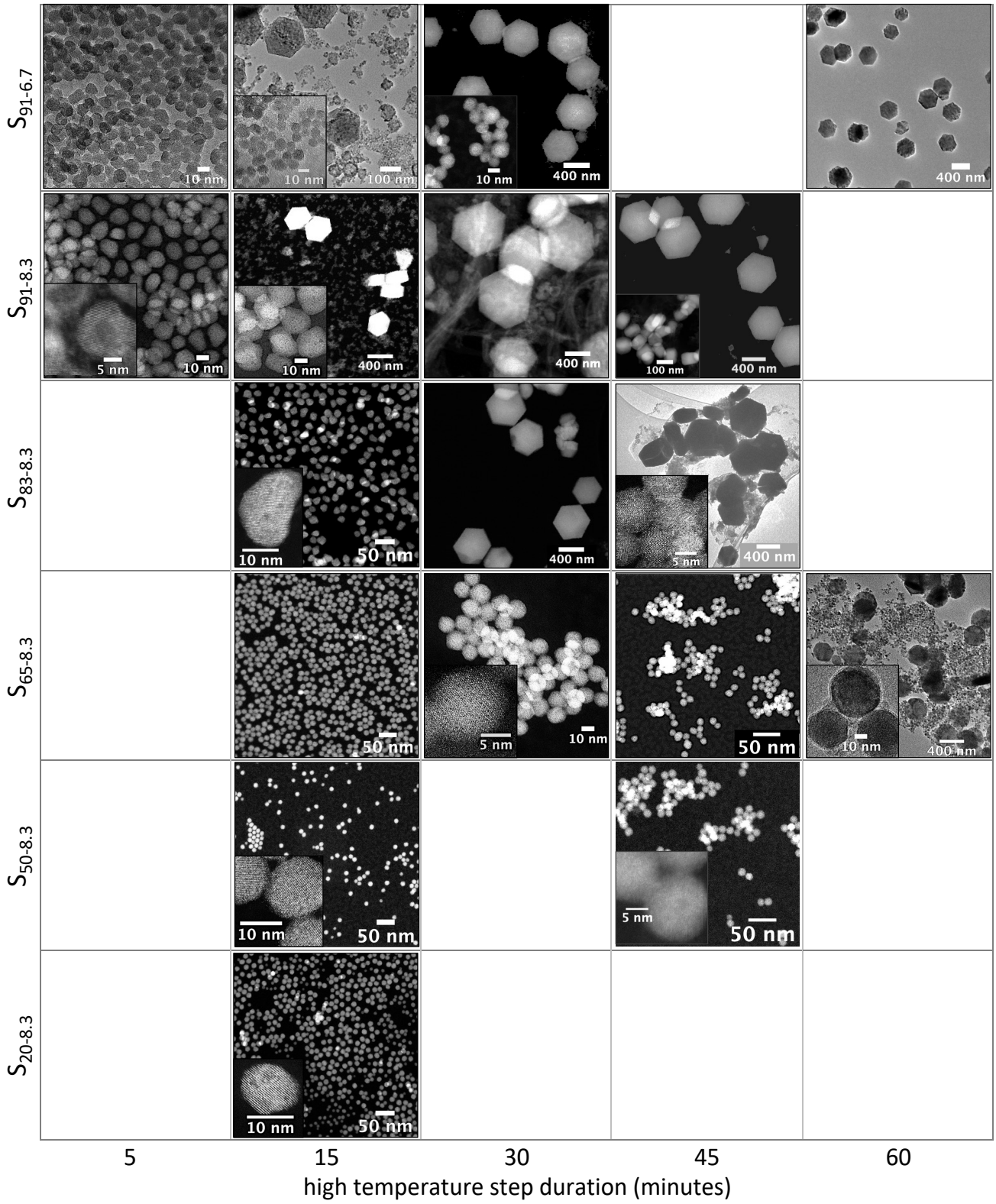

Figure S2: Effect of BEHA concentration and HT step time on UCNP morphology. High Angle Annular Dark Field-Scanning Transmission Electron Microscopy (HAADF-STEM) and bright Field (BF)-TEM images for the full set of experimental conditions presented in this work.

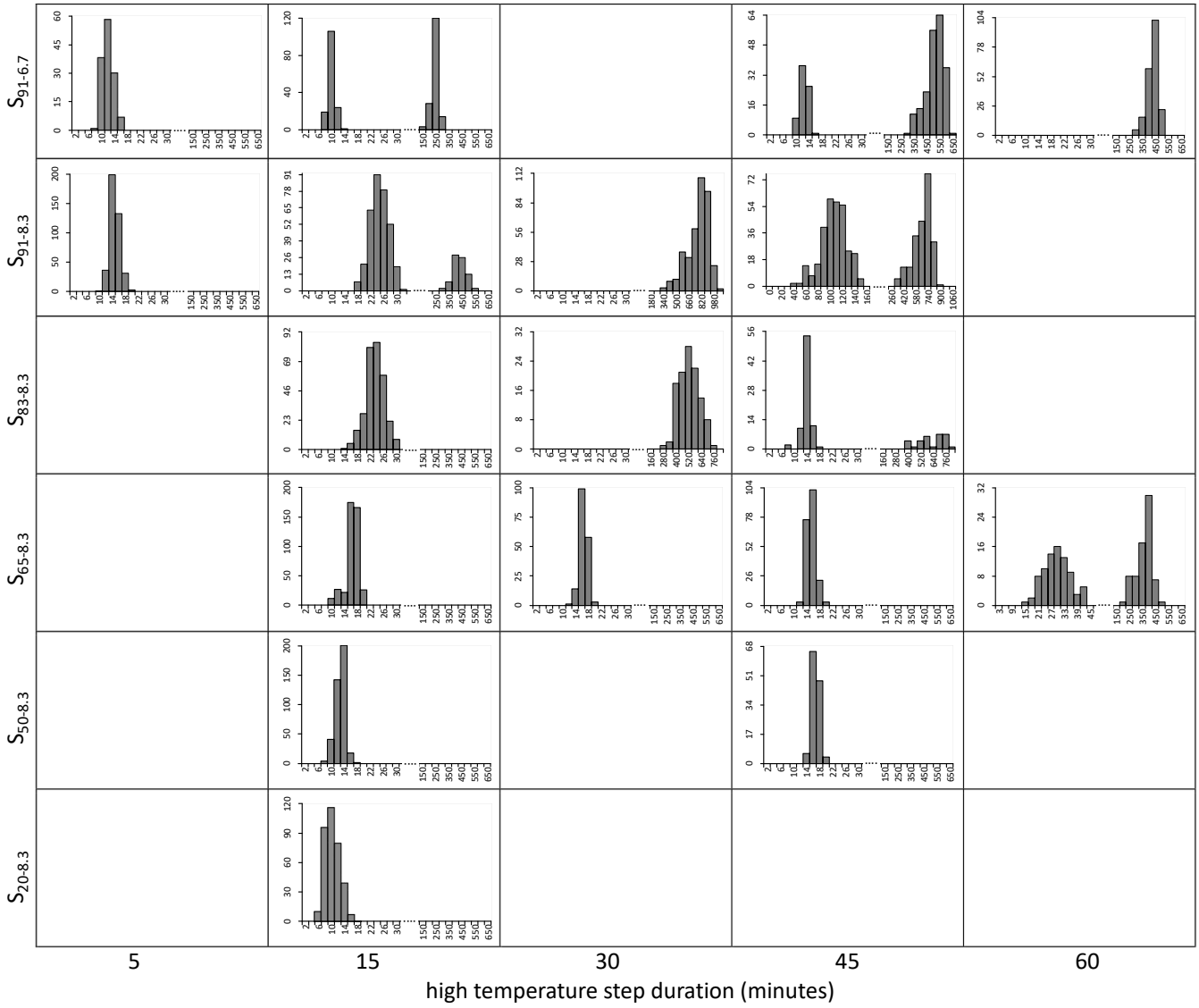

Figure S3: Effect of BEHA concentration and HT step time on UCNP size distributions. Number of particles vs. particle diameter (in nm) measured on HAADF-STEM and (BF)-TEM images for the full set of experimental conditions presented in this work.

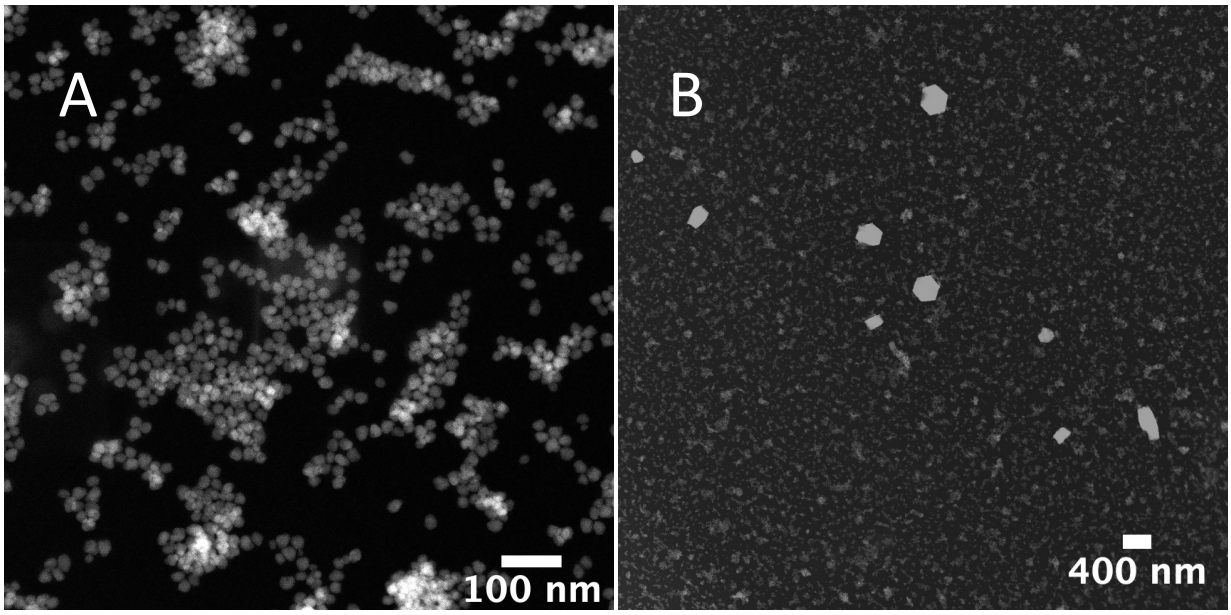

Figure S4. HAADF-STEM images for UCNPs synthesized using a 15-minute HT step, 8.3 mM RE concentration, and 91.7 % v/v BEHA concentration. A) Medium magnification, small UCNPs. B) Low magnification image shows a few large hexagonal particles among the small UCNPs that appear in the image background as lighter spots.

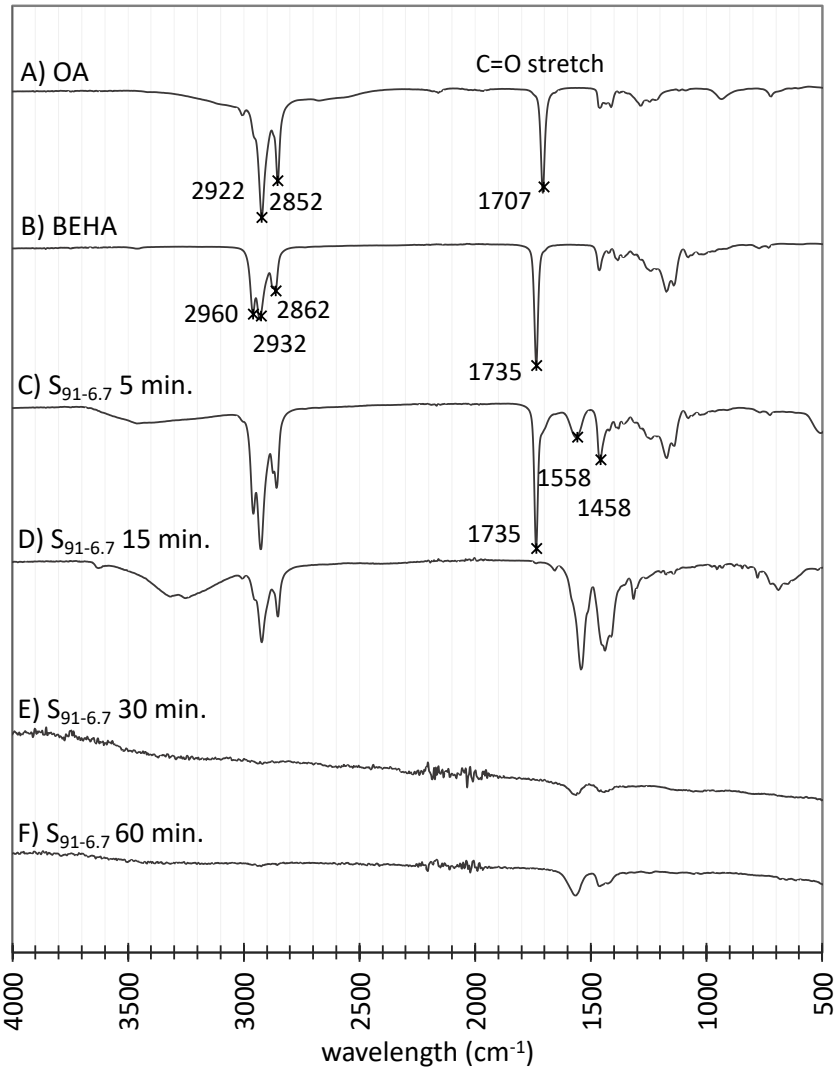

Figure S5. $S_{91\text{-}6.7}$ sample series FTIR-ATR spectra evolution with increasing HT times from 5 to 60 minutes. A) liquid OA. B) liquid BEHA. C) $S_{91\text{-}6.7}$ 5 minutes. D) $S_{91\text{-}6.7}$ 15 minutes. E) $S_{91\text{-}6.7}$ 30 minutes. F) S $S_{91\text{-}6.7}$ 60 minutes. The C-H and C=O stretching peaks of OA and BEHA (marked with asterisks in A and B) gradually disappear with increasing BEHA concentration and longer HT residence time, suggesting that BEHA functions as a stripping ligand.

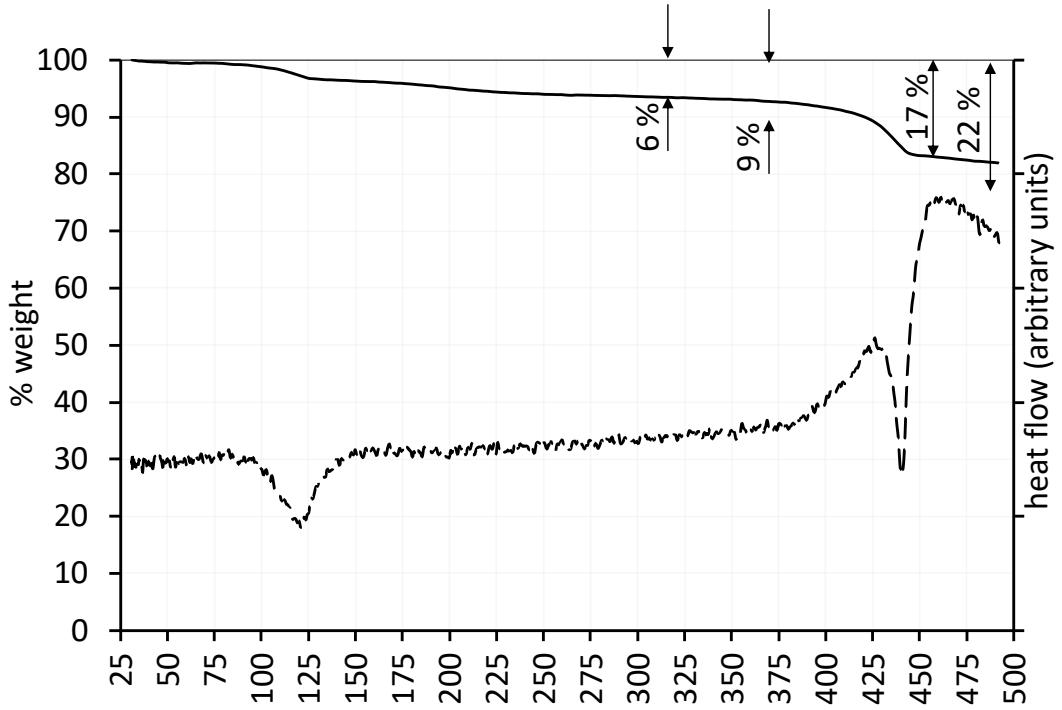

Figure S6: Thermal analysis of the S65-8.3 60 minutes sample. Left axis: thermal gravimetric analysis (TGA), solid line. Right axis: differential scanning calorimetry, dashed line. The first transition is characterized by a DSC endothermic peak that starts around 80 °C, with a TGA mass loss of 6% indicative of residual solvent evaporation. The second transition is characterized by an exothermic followed by a DSC endothermic peak that starts around 400 °C, just before the BEHA boiling point, with an additional TGA mass loss of 11% in the TGA curve, indicative of BEHA thermal decomposition.