XRD patterns of the final products

**Fig. S1.** XRD patterns of the final products recovered after 4 h in comparison with a pattern simulated from ZIF-zni crystal structure data. The compositions of the growth solutions Zn:His:MeOH=1:x:2000 are indicated. The inset compares the most significant range of the XRD patterns.
TR-SLS data of all studied series

Fig. S2. Overview of all HM experiments series. Left graphs represent the evolution of particle mass $M_w$ with time $t$ and the plots on the right side show the evolution of particle size $R_g$ with time $t$. The Zn:Him ratios shown in the figures are indicated in the figure legend.
Estimation of average particle size for intermediate secondary particles after 50 min by XRD

Fig. S3. Comparison of the diffraction peaks in the XRD patterns of the intermediate secondary particles after 50 min (Fig. 16) used for size estimation by Scherrer’s equation. The compositions of the solutions Zn:Him:MeOH = 1:x:2000 are indicated. The red curves are Lorentzian fits. The average size values obtained are 114 nm (x = 4) and 89 nm (x = 6), respectively. The XRD pattern recorded for the 1:2:2000 composition is of very poor quality rendering size estimation impossible. Recording of an XRD pattern as shown in Fig. 16 took 7 h.
Comparison of density per unit area of Zn cations with a terminal ligand position on the (001)/(00-1) and {100} faces.

**Fig. S4.** Drawings showing the Zn cations and their connectivity in the ZIF-zni structure. Upper panel: representations of a (001)/(00-1) face with top view (left) and side view (right). Lower panel: representations of a {100} face with top view (left) and side view (right). The large red and large green circles represent the two crystallographically distinct Zn positions in the top atomic layer of each face, the small orange circles represent Zn positions in layers below the top layers. As can be seen from the side view drawings, all Zn positions in the top layer of a (001)/(00-1) face carry one terminal ligand (this is shown for one representative red and green circle), while only half of the Zn positions in the top layer of one {100} face carry one terminal ligand (this is shown for one representative green circle; the red circles in the top layer have four connectivities like in the bulk phase, that is they do not carry a terminal ligand). The densities per unit area of Zn cations with terminal ligands in the top layers are then 1.449 nm$^{-2}$ and 1.369 nm$^{-2}$ for (001)/(00-1) and {100}, respectively. In the case of a (001)/(00-1) face, which is very rough, half of the Zn positions in the layer (B) below the top layer (A) carry also a terminal ligand, hence the above value of the number density should be multiplied by 3/2. This is not the case for the flat {100} face.