Electronic Supplementary Information for

Post-synthetic modification and chemical modulation of ZIF-8 MOF using 3-mercaptopropionic acid (MPA): a multi-technique study on thermodynamic and kinetic aspects

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This supplementary information provides additional data supporting the study of the effect of 3-mercaptopropionic acid on the nucleation and growth mechanism of ZIF-8 colloidal suspensions at room temperature. This document contains 8 pages, including figures covering the following characterization techniques for ZIF-8 nanocrystals and their pre- and post-synthetic functionalization: Dynamic light scattering, Nitrogen adsorption isotherms, zeta-potential, and isothermal calorimetric titration. This document includes 7 figures, 2 tables, 3 additional references, and this cover page.

Stoichiometric Calculations

20 μL of 10 mM MPA are added to 2 mL of ZIF-8 synthesis mixture with 1:1 volumetric proportion in 25 mM Zn(Ac)$_2$ and 50 mM MeImH methanolic solutions. Therefore, the MeImH:MPA molar ratio is:

$$MeImH{:}MPA = \frac{1^{-3}L \; x \; 50^{-3}Mol/L}{20^{-6}L \; x \; 10^{-3}Mol/L} = \frac{250}{1}$$
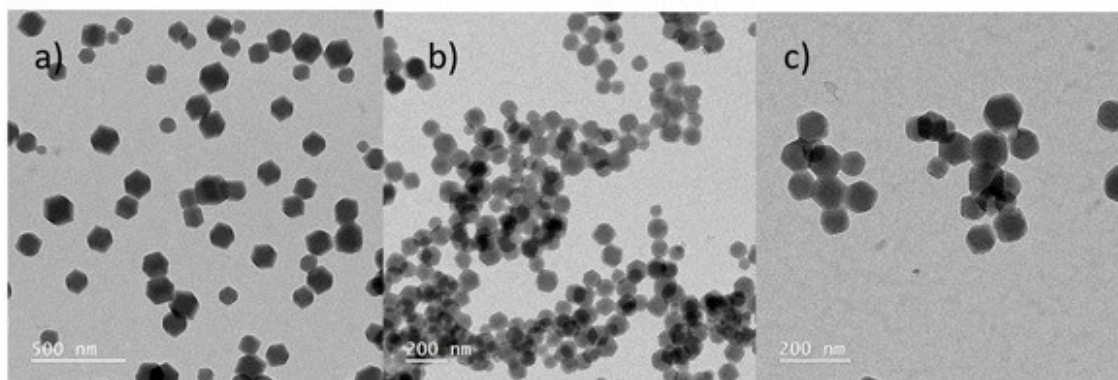

Figure S1. TEM images of ZIF-8 crystals a) before reaction b-c) after reaction with MPA.
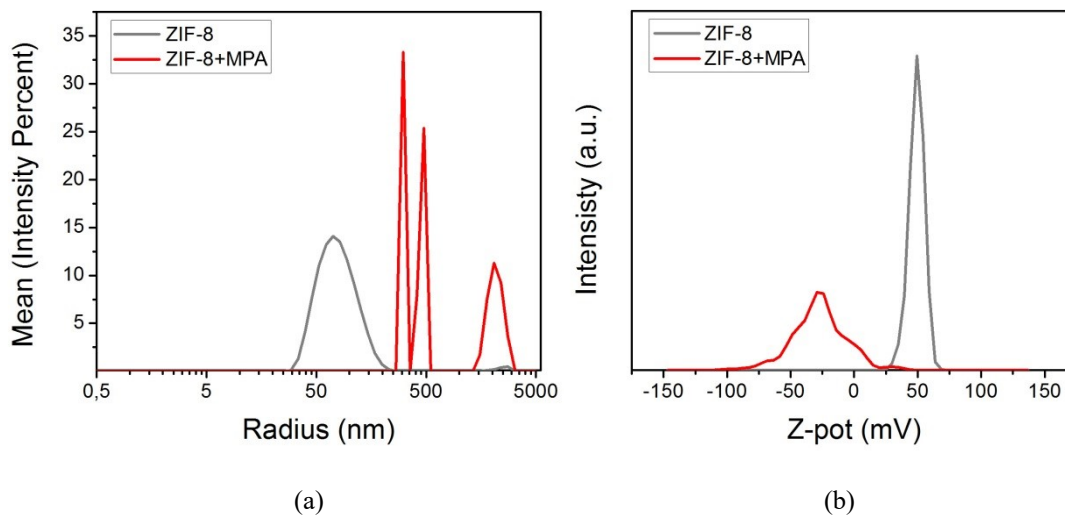

(a)

(b)

Figure S2. (a) DLS size measurement and b) Z-potential measurements for ZIF-8 and ZIF-8+MPA.
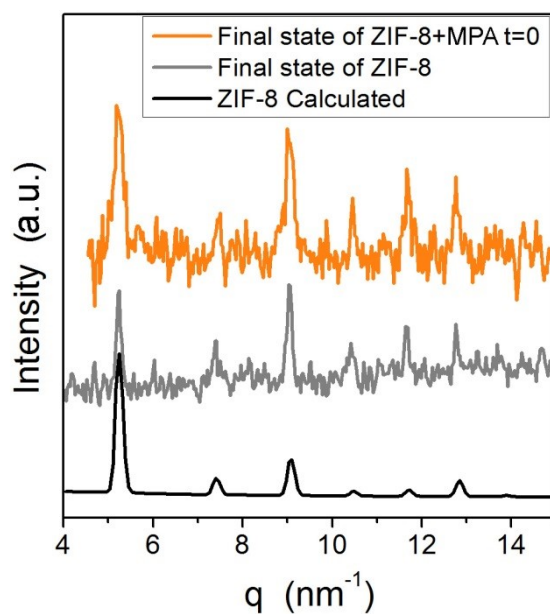
Figure S3. WAXS pattern of ZIF-8 and ZIF-8+MPA t=0 nanoparticles obtained for final stage of colloidal synthesis. The theoretical diffraction pattern was calculated using ZIF-8 available data file from Cambridge Crystallographic Data Centre (CCDC).
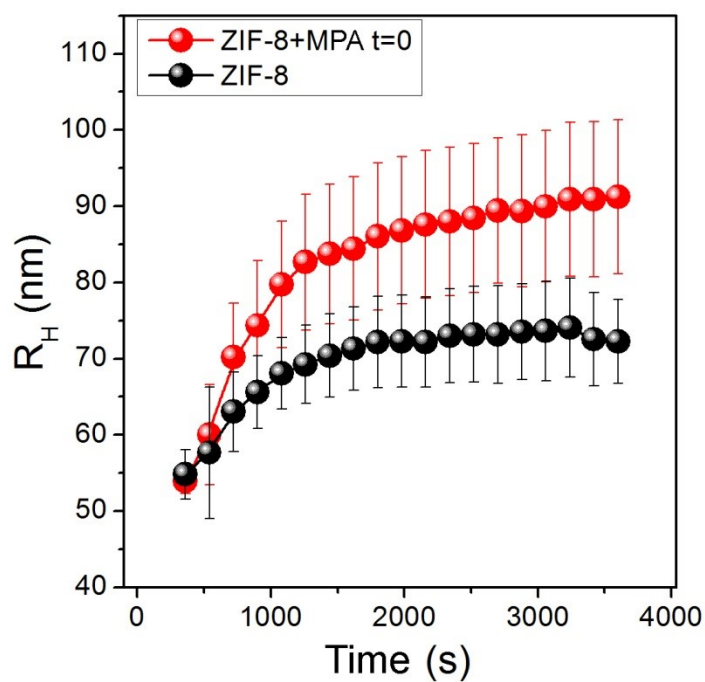

Figure S4. Evolution of the hydrodynamic radius of ZIF-8 (black) and ZIF-8+MPA t=0 obtained via DLS.

Fitting the SAXS and DLS data using the following appropriate empiric models confirms that the growth of ZIF-8 would be controlled by the diffusion of the precursors:[1]

Mononuclear growth:

$$\frac{1}{r} = \frac{1}{r_0} - k_m(C)t \tag{S1}$$

where k_m depends on the solut concentration.

Polinuclear growth:

$$r = r_0 + k_p t \tag{S2}$$

Growth controlled by diffusion of precursors:

$$r^2 = r_0^2 + k_D t \tag{S3}$$

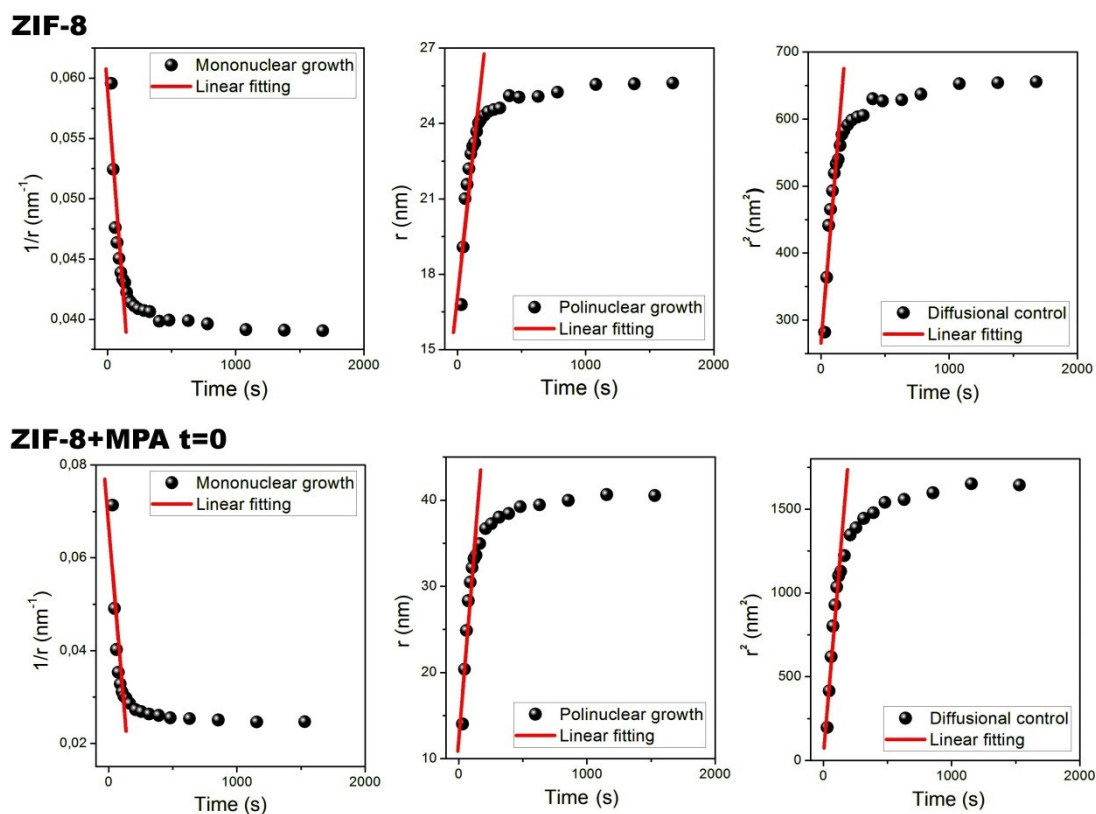where k_D depends on the diffusion coefficient.

Figure S5. Linear fitting for the experimental results of the ZIF-8 and ZIF-8+MPA t=0 growth determined via SAXS using different empiric models (equations 3.10-3.12).
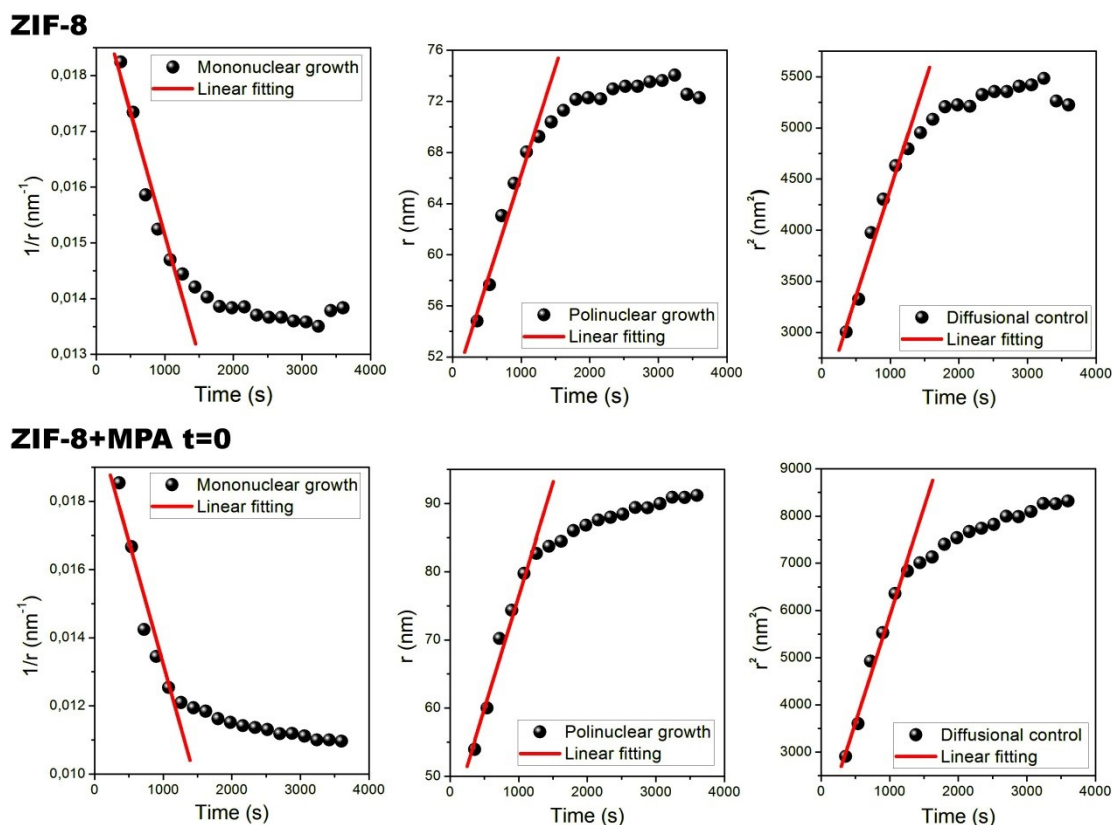
Figure S6. Linear fitting of the experimental data obtained for the ZIF-8 and ZIF-8+MPA t=0 growth determined via DLS using different empiric models (equations 3.10-3.12).

Table S1. Values of the correlation coeficients of the fittings done for the ZIF-8 and ZIF-8+MPA t=0 growths obtained from the SAXS and DLS measures, using the empiric models proposed (equations S2-S5).

ZIF-8		
Model	**R^2 (SAXS)**	**R^2 (DLS)**
Mononuclear	0.78971	0.93998
Polinuclear	0.84081	0.96048
Diffusional control	0.87957	0.96877
ZIF-8+MPA t=0		
Mononuclear	0.7241	0.92687
Polinuclear	0.88977	0.96844
Diffusional control	0.94134	0.98159

Table S2. Summary of the elemental proportions determined through processing of the XPS spectra for ZIF-8+MPA t=0. The theoretical S:Zn% was calculated assuming the thiol homogenously distributed in the whole ZIF-8 crystals.

ZIF-8+MPA t=0			
Name	**ratio Zn:N:C**	**Experimental S:Zn%**	**Theoretical S:Zn%**
Zn 2p	1		
N 1s	3.53		
C 1s	12.97		
S 2p		17.68	0.8

N2 adsorption experiments

Bare (Fig. S7-upper panel) and MPA-modified (Fig. S7-lower panel) ZIF-8 samples were exchanged with fresh solvent and dried under vacuum at 200 ºC for 12 hours. BET surface area was determined from the isotherms (duplicated experiments) in the p/p_0 range which ensured fulfillment of Rouquerol´s criteria (0,005 - 0,07) using the software included in the ASAP 2020 apparatus.[2] Regions associated with hysteresis loop are displayed in an enlarged area in the insets.
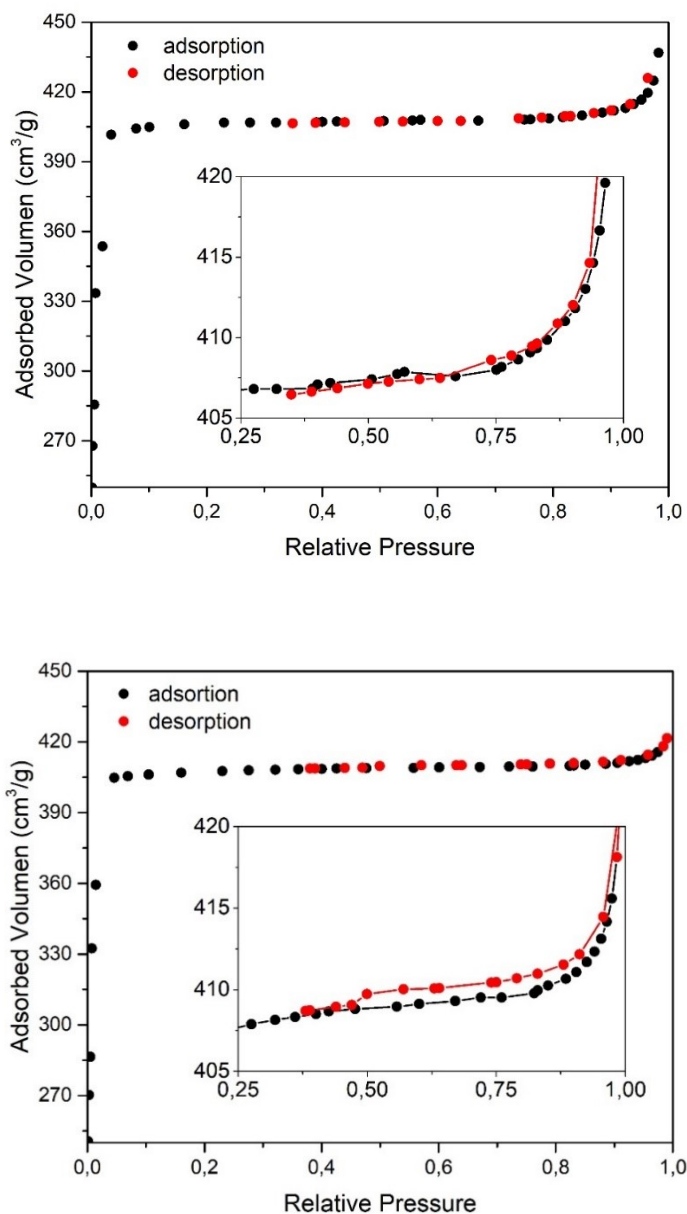

Fig. S7. Nitrogen adsorption isotherm corresponding to bare ZIF-8 (**Top**) and MPA-modified material **(bottom).** Both isotherms are typical for microporous materials, but insets show the appearance of a hysteresis loop between adsorption and desorption branches ascribable to the formation of mesopores arising from coordinative etching upon MPA modification.

Calculations

First of all, an estimation of the energy involved in the Zn-carboxylic acid coordination process would not be possible if ITC experiments would be carried during ZIF-8 formation (i.e., if MPA would be included with MOF precursors) due to the considerable high enthalpies related to nucleation/growth process (around 70 kJ/mol).[3]

Taking into account that the moles of MPA are 200 μL x 0.8190 mM $=$ **1.638x10^{-7} moles**, it is important to estimate the moles of unsaturated Zn^{2+} ions on the ZIF-8 crystal surface. These depend on the crystalline phase exposed on the crystal surface and the size of the crystals. In this case, we will estimate the number of Zn^{2+} moles on the crystal surface assuming that the crystals are spherical and they expose the (100) crystal plane (which contains 4 Zn^{2+} ions).[4] Additionally, we will consider that the lattice parameter of ZIF-8 unit cell ($a = 16.992$ Å) and this has 12 Zn^{2+} ions ($Zn_{12}N_{48}C_{96}$).[5]

How many Zn^{2+} ions are there on the ZIF-8 crystal surface?

$$\frac{Sphere\ area}{Unit\ cell\ area} \cdot \frac{4\ Zn^{2+}}{6.023x10^{23}}\ moles$$

For ZIF-8 crystals ($r = 50$ nm): 7.2x10^{-20} moles Zn^{2+}

How many ZIF-8 particles are there into the colloidal dispersion?

$$\frac{7.9\ mM\ x\ 1.456\ mL}{\frac{Sphere\ volume}{Unit\ cell\ volume} \cdot \frac{12\ Zn(HmimH)_2}{6.023x10^{23}}\ moles}$$

For ZIF-8 crystals ($r = 50$ nm): 5.4x10^{12}

So, **the number of Zn^{2+} moles on the ZIF-8 surface particles** is:

For ZIF-8 crystals ($r = 50$ nm): **3.9x10^{-7} Zn^{2+} moles**

This value is slightly lower than the number of MPA moles used (1.638x10^{-7} moles).

References

1   A. P.C., *Introduction to Sol-Gel Processing (The International Series in Sol-Gel Processing: Technology & Applications)*, 1998.

2   D. A. Gómez-Gualdrón, P. Z. Moghadam, J. T. Hupp, O. K. Farha and R. Q. Snurr, *J. Am. Chem. Soc.*, 2016, **138**, 215–24.

3   J. Cravillon, C. A. Schröder, H. Bux, A. Rothkirch, J. Caro and M. Wiebcke, *CrystEngComm*, 2012, **14**, 492–498.

4   Z. Li and H. C. Zeng, *Chem. Mater.*, 2013, **25**, 1761–1768.

5   F. Paquin, J. Rivnay, A. Salleo, N. Stingelin and C. Silva, *J. Mater. Chem. C*, 2015, **3**, 10715–10722.