Supporting information

for

Shape control in ZIF-8 nanocrystals and metal nanoparticle@ZIF-8 heterostructures

Guangchao Zheng,[a,b] Zhuwen Chen,[a] Kadir Sentosun,[c] Ignacio Pérez-Juste,[b] Sara Bals,[c] Luis M. Liz-Marzán,[b,c,d] Isabel Pastoriza-Santos,[b] Jorge Pérez-Juste,*[b] Mei Hong*[a]

[a] Guangdong Provincial Key Laboratory of Nano-Micro Materials Research, School of Chemical Biology & Biotechnology, Peking University Shenzhen Graduate School, Shenzhen 518055, China.

[b] Departamento de Química Física and CINBIO, Universidade de Vigo, 36310, Vigo, Spain.

[c] EMAT-University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium,

[d] Bionanoplasmonics Laboratory, CIC biomaGUNE, 20009 Donostia-San Sebastián, Spain.

[e] Ikerbasque, Basque Foundation for Science, 48013 Bilbao, Spain.

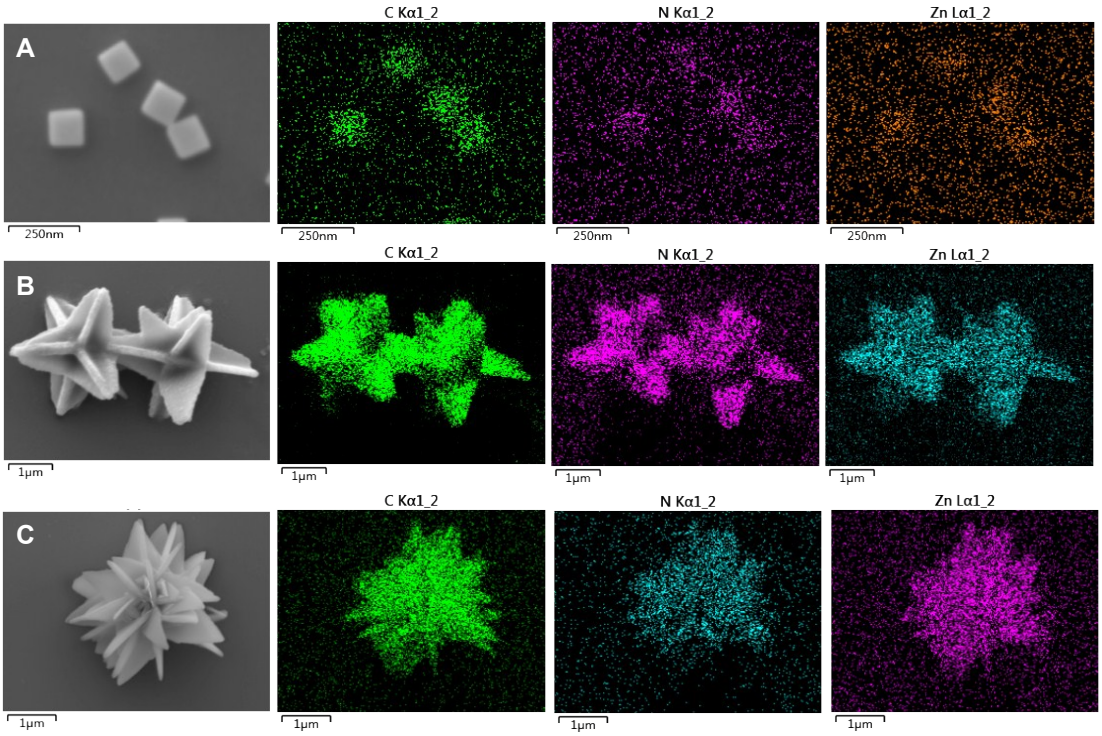


Figure S1. Representative SEM images and their corresponding EDX mappings of ZIF-8 nanocrystals with a cubic (A), flake (B) and flower-like (C) morphologies.

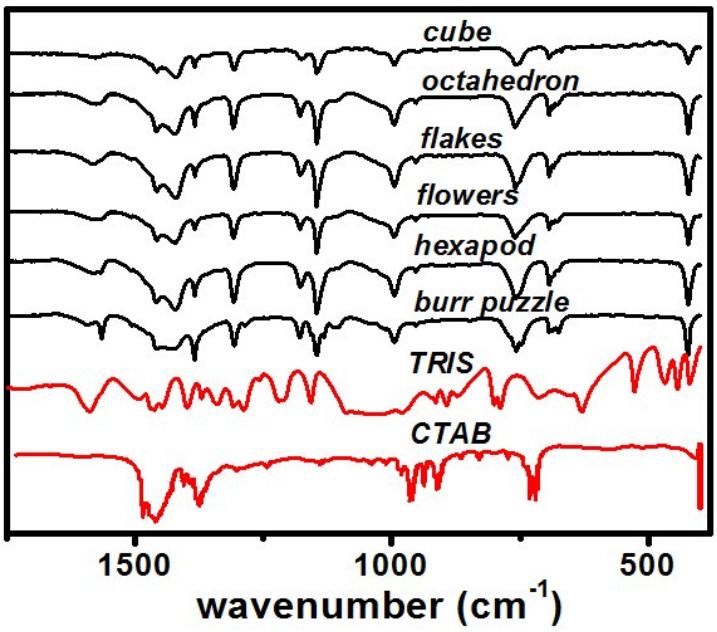


Figure S2. FTIR spectra of the different ZIF-8 nanocrystals; the absorption band at 1584 cm^{-1} was due to C=N stretching, whereas bands between 1350-1500 cm^{-1} can be assigned to the entire ring stretching.[1] The peak at 425 cm^{-1} shows the distinct stretching vibration of Zn-N. For comparison the FTIR spectrum of TRIS is also included, dominated by a broad band located at 1000 – 1065 cm^{-1} attributed to the vibrational band of CO.[2]

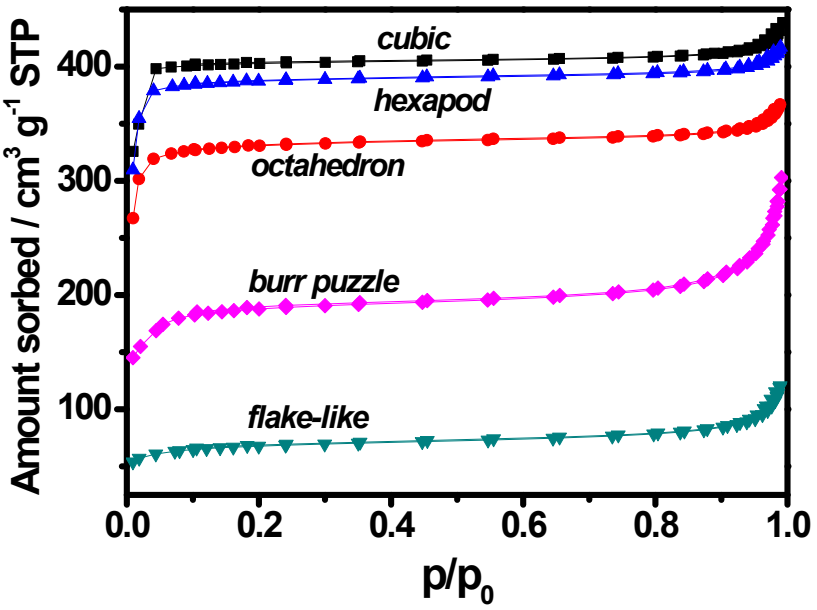


Figure S3. (A) N_2 physisorption at the liquid nitrogen temperature for the different ZIF-8 nanoparticles. The surface areas were calculated adopting the BET model.

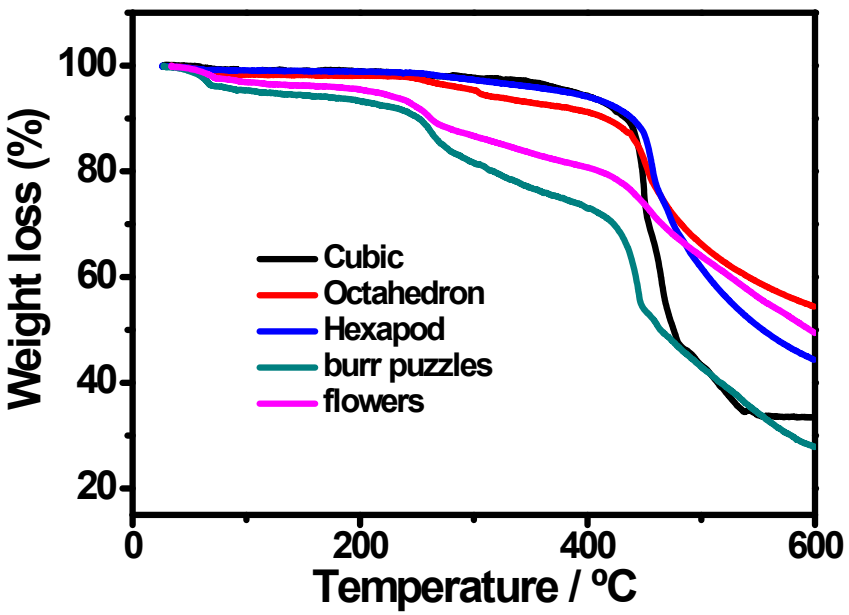


Figure S4. TGA curves of the different ZIF-8 nanocrystals. In the case of cubic, octahedron and hexapod-shaped nanoparticles the TG curves exhibit a small gradual mass loss (below 5 %) up to ca. 400 °C, which could be attributed to the removal of guest molecules (e.g., methanol) from the cavities and some species (e.g., Hmim) from the surfaces of the nanocrystals. This temperature range is restricted to 200 ºC in the case of flake-like and burr puzzle nanoparticles. Additionally, in all cases a endothermic mass loss (between 50 to 65 %) is observed up to ca. 600 °C which corresponds to the removal of the organic linker molecules. Overall, the thermogravimetric analysis reveals that, in air, the nanocrystals are stable at least up to 200 ºC and that there is not influence of CTAB or TRIS in the thermal stability of the ZIF-8 nanocrystals.

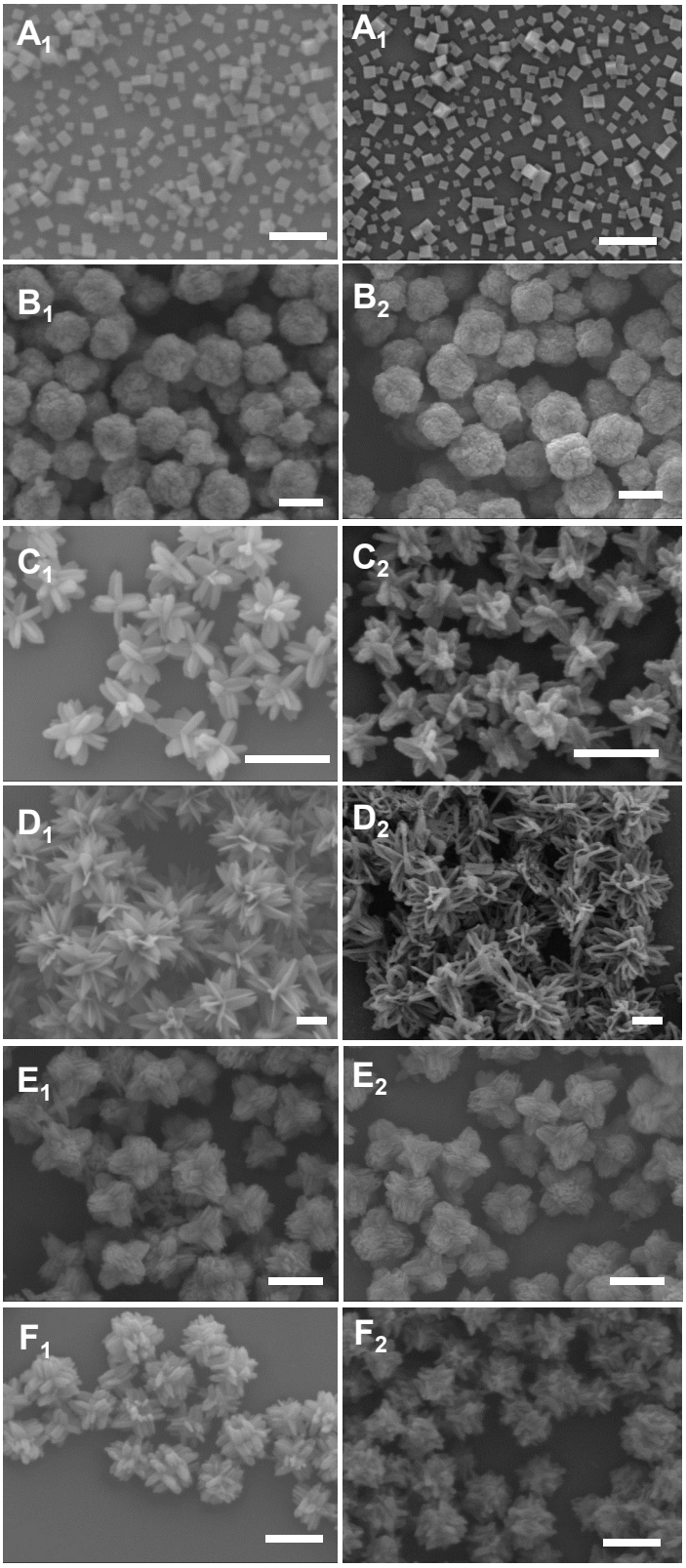


Figure S5. Representative SEM images of ZIF-8 nanocrystals as synthesized (1) and after 7 days upon storage in methanol (2): A) cubic, B) octahedron, C) flake-like, D) flower-like, E) hexapod, and F) burr puzzle. Scale bars represent 1 μm.

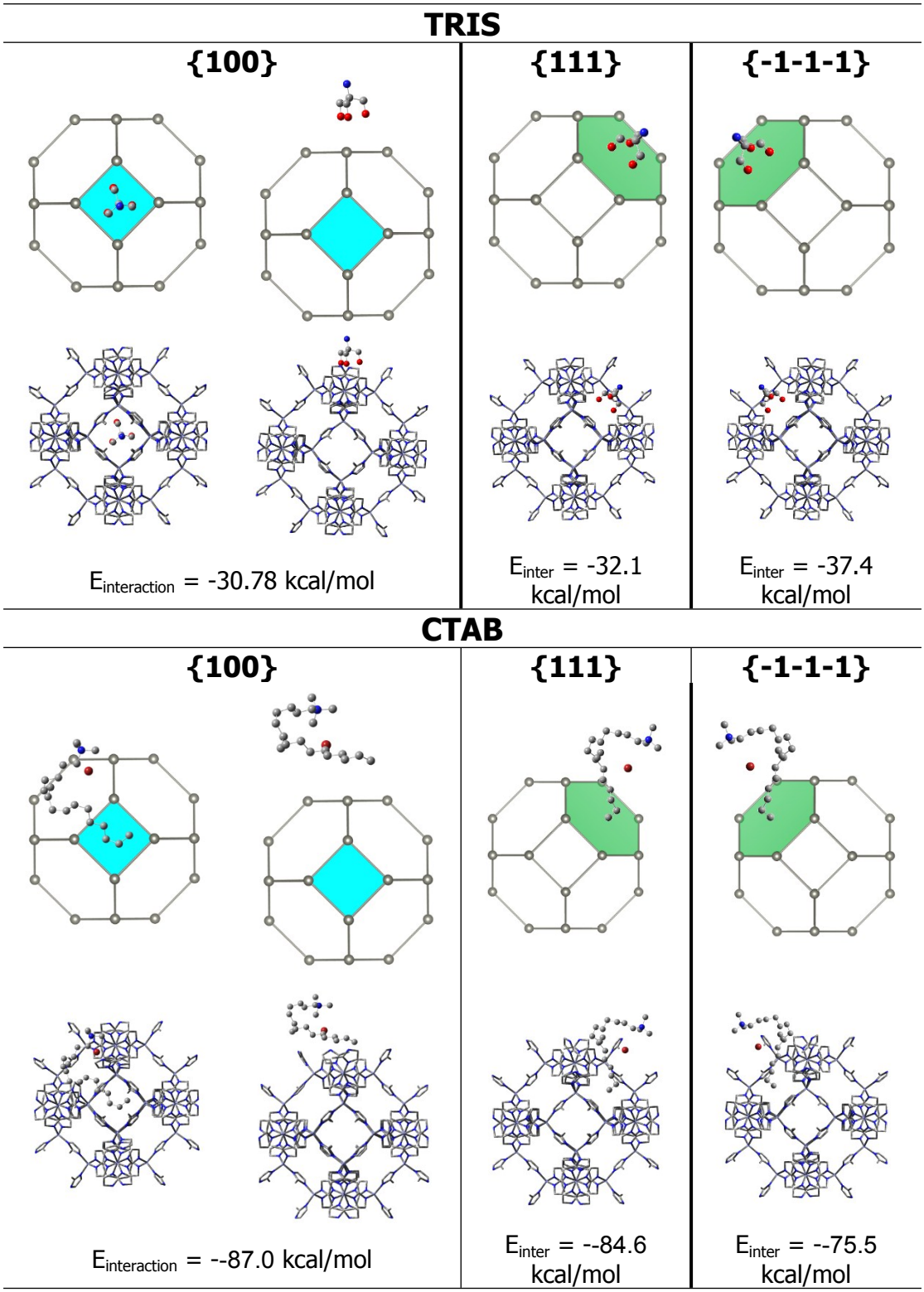
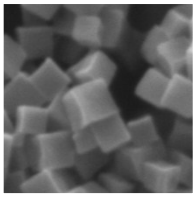
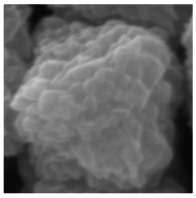
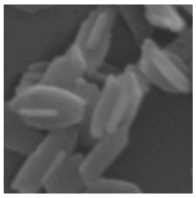
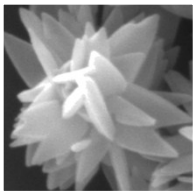
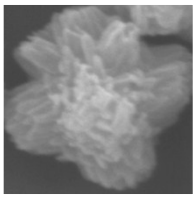
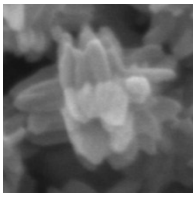


Figure S6. Minimized intermolecular interactions between the 100 and 111 facets of ZIF-8 and a unit of TRIS or CTAB obtained by semiempirical methods. Interactions energies (in kcal/mol) have been calculated as $E_{interaction} = E_{complex} - (E_{ZIF8} + E_{CTAB}/E_{TRIS})$. See text and experimental section for details.

Table S1. Summary of ZIF-8 morphologies obtained in the presence of CTAB or/and TRIS and their corresponding BET surface areas determined by the BJH adsorption model.

Entry	CTAB	TRIS	Morphology	SEM	Surface Area m^2/g	Yield / %[a]
A	(0.07-0.35) mM	--	cubic		1192.6	39.6
B	--	10mM	octahedral		986.3	42.1
C	--	50mM	flakes		307	41.5
D	--	100mm	Flowers			25.0
E	0.07 mM	10mM	hexapod		1150.2	40.9
F	0.07 mM	50mM	burr puzzle		1282	42.4

[a] To estimate the yield in each case the consumed and remained amounts of $Zn(NO_3)_2.6H_2O$ and 2-methylimidazole were calculated by using initial amounts of materials and the amount of ZIF-8 synthesized. Considering the reaction of the synthesis;

$$6\ Zn(NO_3)_2.6H_2O + 12\ C_4H_6N_2 \rightarrow Zn_6N_{24}C_{48}H_{60}$$

Taking into account that Mw ($Zn_6N_{24}C_{48}H_{60}$) = 1365.51 g/mole the maximum amount of ZIF-8 can be estimated as

$$ZIF\text{-}8_{max} = 1\ mL\ Zn(NO_3) \times 24 mM Zn(NO_3) \times \frac{1\ mole\ ZIF\text{-}8}{6\ mole\ Zn(NO_3)} \times \frac{1365.51\ g}{1\ mole\ ZIF\text{-}8} = 0.0328\ g$$

After washing and drying the yield can be estimated as

$$Yield,\ \% = \frac{Obtained\ amount\ of\ ZIF\text{-}8}{Maximum\ amount\ of\ ZIF\text{-}8}$$

- Supporting video SV1. 3D volume representation of a Au@Ag nanorods encapsulated within cubic ZIF-8 nanocrystal demonstrating the core-shell configuration.

- Supporting video SV2. 3D volume representation of a Au@Ag nanorods encapsulated within burr-puzzle ZIF-8 nanocrystal demonstrating the core-shell configuration.

References

[1] N. A. H. M. Nordin, A. F. Ismail, A. Mustafa, P. S. Goh, D. Rana, T. Matsuura, *RSC Adv.* **2014**, *4*, 33292-33300.

[2] S. Schroetter-Dirks, D. Bougeard, *J Mol Struct* **2003**, *661*, 109-119.