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Self-assembly of polyhedral metal–organic framework particles into three-dimensional ordered superstructures

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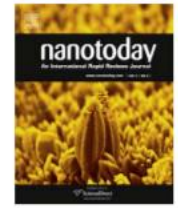

REVIEW

Superlattices with non-spherical building blocks

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LETTERS

Dense packings of the Platonic and Archimedean solids

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INTRODUCTION

- Spherical colloidal particles are known to form self-assembled superstructures and tend to pack into the entropically favoured face-centred cubic (fcc) arrangement.

- Recently, the self-assembly of non-spherical polyhedral particles can be considered as a viable method to diversify possible packing geometries

- Colloidal crystalline polyhedral MOF particles, **zeolitic imidazolate framework-8 (ZIF-8)** and **Universitetet i Oslo-66 (UiO-66)** can be synthesized with the required size and shape homogeneity to subsequently self-assemble into well-ordered three-dimensional superstructures.

- Self-assembled spherical colloidal particles (mainly silica, polystyrene and acrylates) can form photonic crystals because they tend to order into superstructures capable of reflecting. light at specific wavelengths and directions (photonic bandgap) due to the periodic refractive index distribution they create.

- Here, the photonic bandgap of the MOF-based superstructures can be tuned by controlling the size of the MOF particles and is also responsive to the sorption of guest substances.

Synthesis of Truncated Rhombic Dodecahedral ZIF-8 particles

- Highly monodisperse colloidal TRD ZIF-8 particles in water were fabricated and stabilized by using **CTAB as a cationic surfactant and a capping agent**.

- ZIF-8 is a porous MOF made of Zn(II) ions and 2-methylimidazolate (2-MiM) linkers that exhibits a **sodalite-type structure**.

- ZIF-8 crystalization path :

  Cubic Shaped seed ➔ TRD particles ➔ Rhombic Dodecahedral (RD) particles
  (thermodynamicaly stable)

- CTAB facilitates TRD ZIF-8 synthesis as it selectively attaches to {100} facets

- Size ranging from 178 ± 8 nm to 227 ± 10 nm was synthesized on controlling the amount of CTAB and 2-MiM

- X-Ray powder diffraction proved crystalline ZIF-8

- Nitrogen physical sorption measurements on the ZIF-8 particles validated their microporosity.

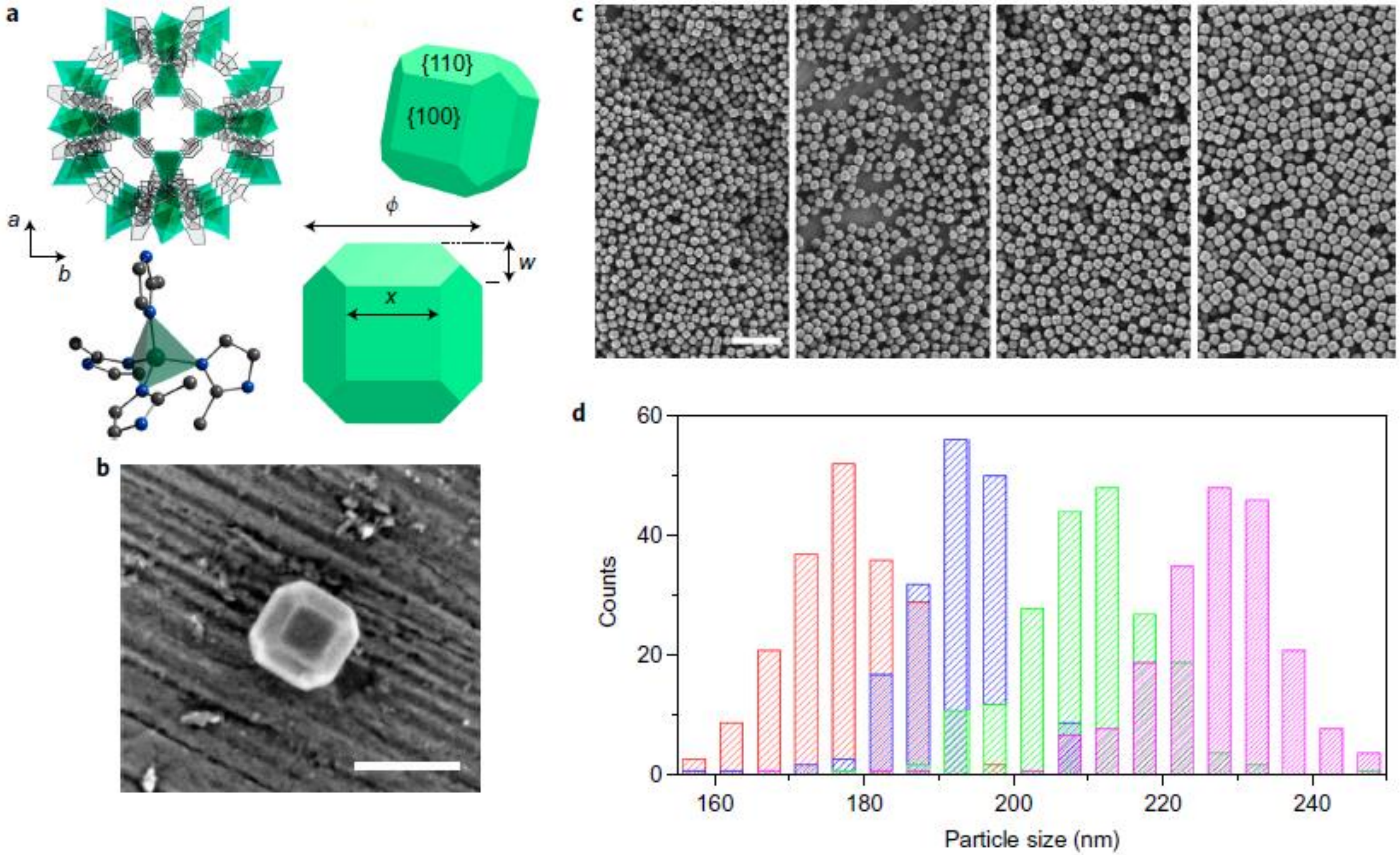
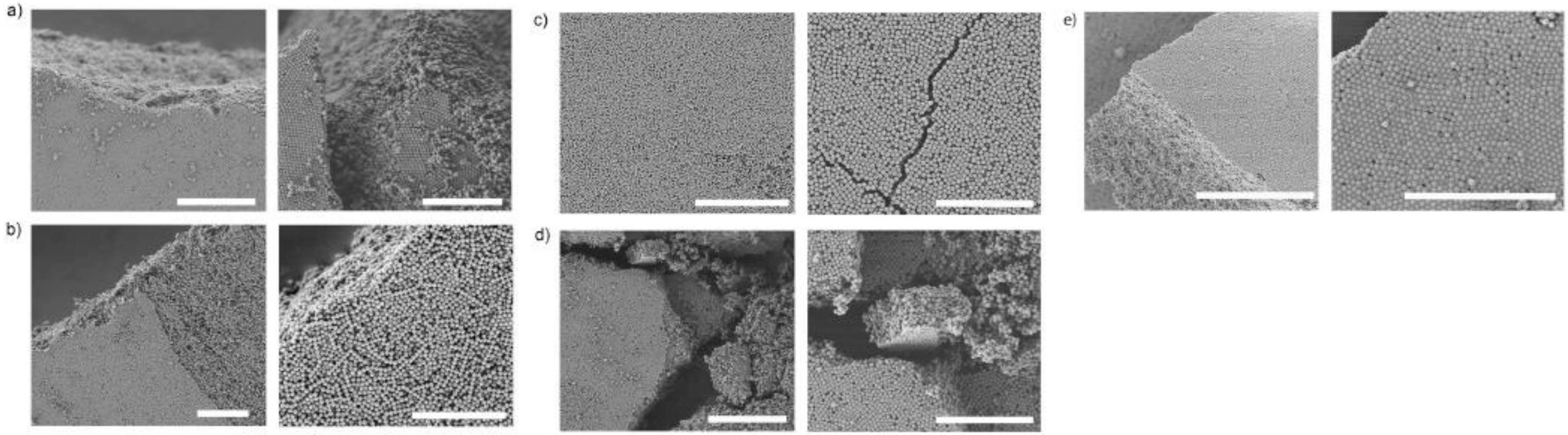


Figure 1 | Structure and characterization of the TRD ZIF-8 particles. **a**, Representation of the crystal structure of ZIF-8 showing that it is formed by the connection of tetrahedral Zn(II) ions (in green) through 2-methylimidazolate (2-MiM) linkers (in grey, top left). Bottom left: environment around one zinc centre. Atom colour code: Zn, green; C, grey; N, blue. Right: schematic illustrations of the ZIF-8 TRD particles, showing the {110} and {100} facets (top) and highlighting: particle size ϕ; edge length x of the {100} square facets; and chamfer w (bottom). **b**, Representative FE-SEM image of a single TRD ZIF-8 particle. **c**, Representative FE-SEM images of TRD ZIF-8 particles of different sizes. From left to right: 178 ± 8 nm, 193 ± 8 nm, 210 ± 10 nm and 227 ± 10 nm. **d**, Size-distribution histograms of TRD ZIF-8 particles of different sizes: red, 178 ± 8 nm; blue, 193 ± 8 nm; green, 210 ± 10 nm; and purple, 227 ± 10 nm. Scale bars: 200 nm (**b**) and 1 µm (**c**).

Self-assembly of TRD ZIF-8 particles

- A droplet of an aqueous colloidal solution of the particles (100 mg ml^{-1}) was placed on a clean glass surface and then, the surface was incubated in an oven at 65 °C until the droplet was dried.
- Other methods attempted

Representative FE-SEM images of the self-assembled superstructures obtained using different techniques: a) evaporation at RT; b) evaporation at 100 ^{o}C; c) spin coating; d) dip coating; and e) vertical deposition. Scale bars: 10 µm (left column) and 5 µm (right column).



- Upon self-assembly, the TRD ZIF-8 particles adopted the **densest rhombohedral packing**, with a packing fraction of 0.86 (Figure 3)

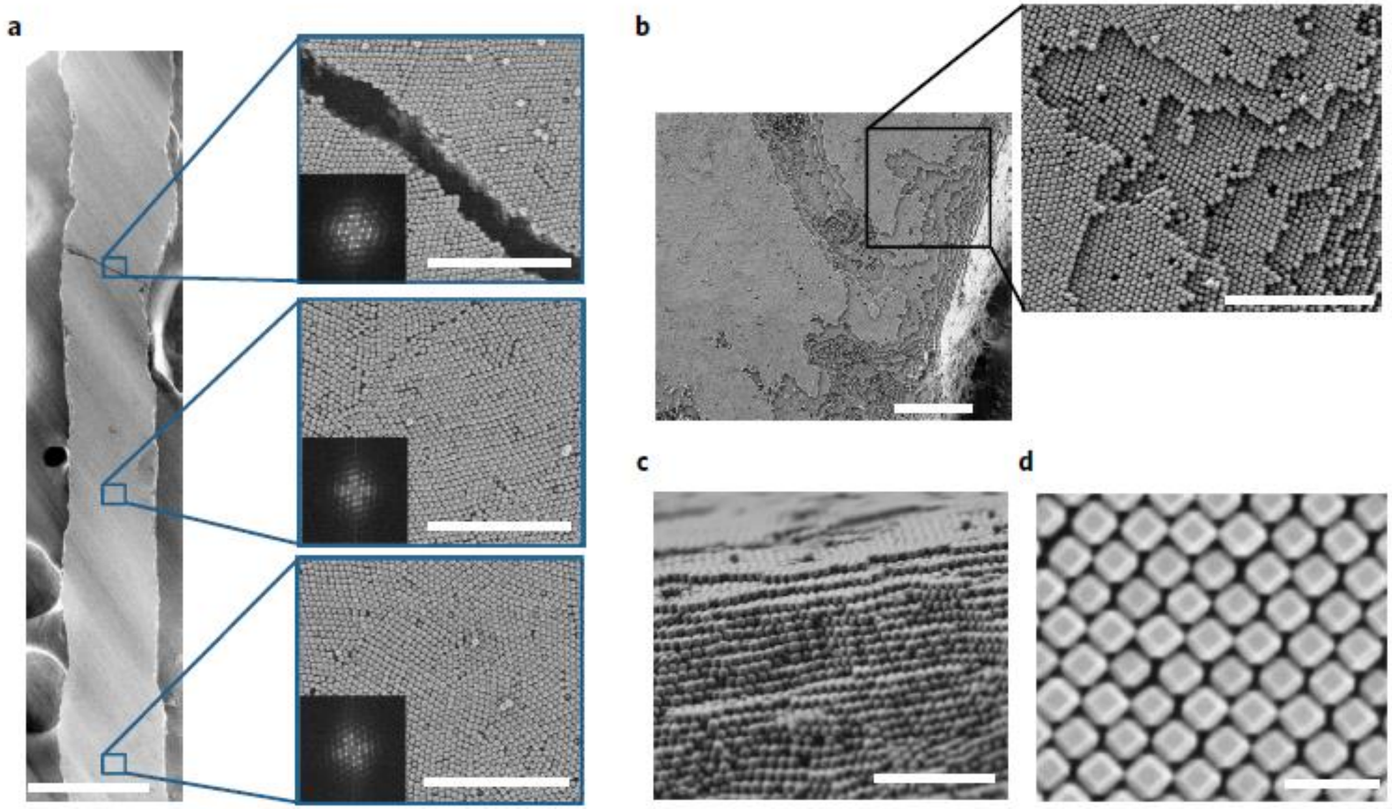


Figure 2 | Ordered rhombohedral self-assembled superstructures. Representative FE-SEM images of a self-assembled superstructure made of TRD ZIF-8 crystals (size 210 ± 10 nm). **a**, Low-magnification image of a self-assembled superstructure that extends over 1 mm. The three magnified sections reveal that the rhombohedral lattice is maintained across the self-assembled superstructure. Note here that—as in any other superstructure made of self-assembled particles—the ordering of TRD ZIF-8 crystals reveals domains with misfit dislocations and point defects. Insets: Fourier transforms of these sections showing different grain orientations. **b**, Edge of a self-assembled superstructure, showing order in the three dimensions. **c**, Cross-section of the self-assembled superstructure. **d**, Zoom of the packing structure. Scale bars: 200 μm (**a**), 5 μm (**a**, insets), 10 μm (**b**), 1 μm (**b**, inset), 2 μm (**c**) and 500 nm (**d**).

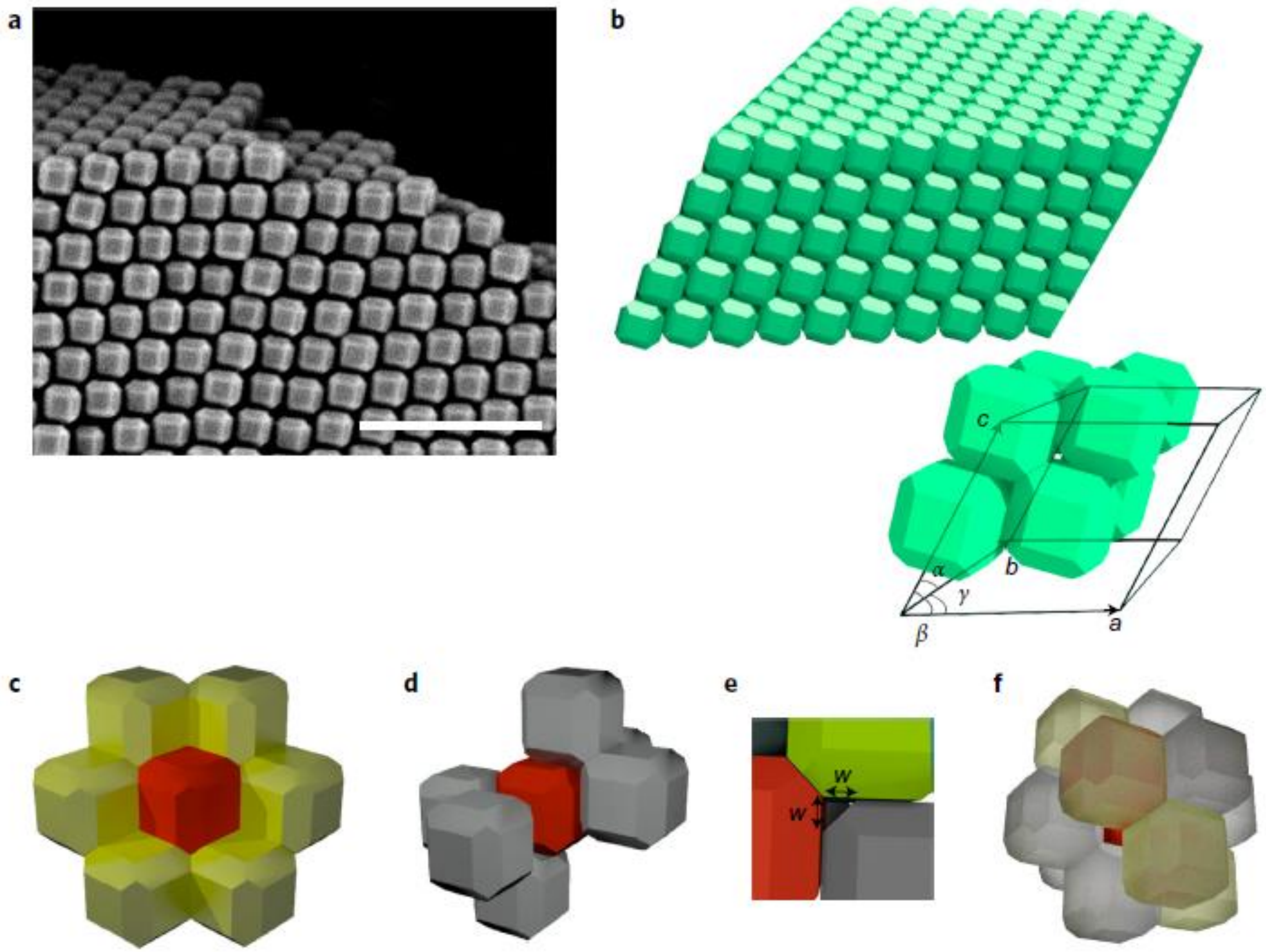
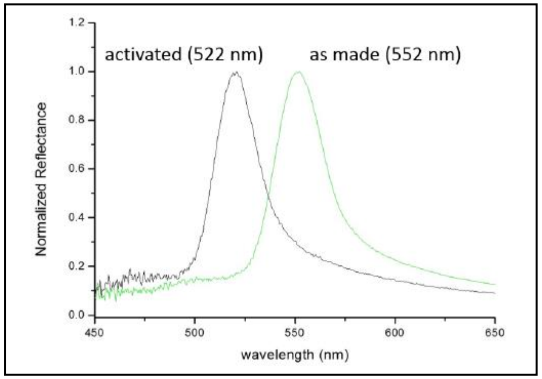


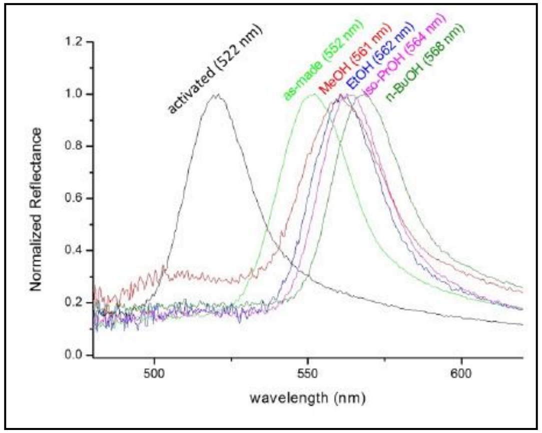
Figure 3 | Computer simulation and FE-SEM image of the formation of the densest rhombohedral lattice. **a**, Representative FE-SEM image of a cross-section of the self-assembled superstructure, showing the rhombohedral lattice. **b**, Densest packing obtained from Floppy-Box Monte Carlo simulations, confirming the same type of rhombohedral lattice obtained experimentally. Bottom right: unit cell of the rhombohedral lattice. **c–f**, Schematics showing the connectivity of a single TRD ZIF-8 particle in the rhombohedral lattice: six TRD particles perfectly aligned through the {110} facets (**c**); six TRD particles aligned through the {100} facets (**d**); representation showing the shift in two directions of these latter connections (**e**); combined 12 TRD particles aligned to a single TRD particle (**f**). Scale bar in **a**: 1 μm.

Photonic Crystal Properties

- **Microporosity of MOFs** highly favours the use of these photonic structures for the development of sensing applications, because the adsorption of species in the MOF pore network can change their refractive index, resulting in a pronounced shift in the photonic bandgap spectral position λ_c.
- **Activation of Porous MOF** : TRD ZIF-8 was heated at 260 ^oC driving out guest water
- **Activated photonic crystal :** λ_c = shorter wavelengths (from 552 to 522 nm), may be due replacement of water molecules with air (Optical reflectance at $\theta = 0^o$)



- **Exposure :** to different alcohols and water vapour.
  Red shift for alcohols and none for water.



- **Conclusion:** Thus, the replacement of water molecules with air in the pores of ZIF-8 at relatively low pressures changes the refractive index of the photonic crystal, causing the bandgap to shift.

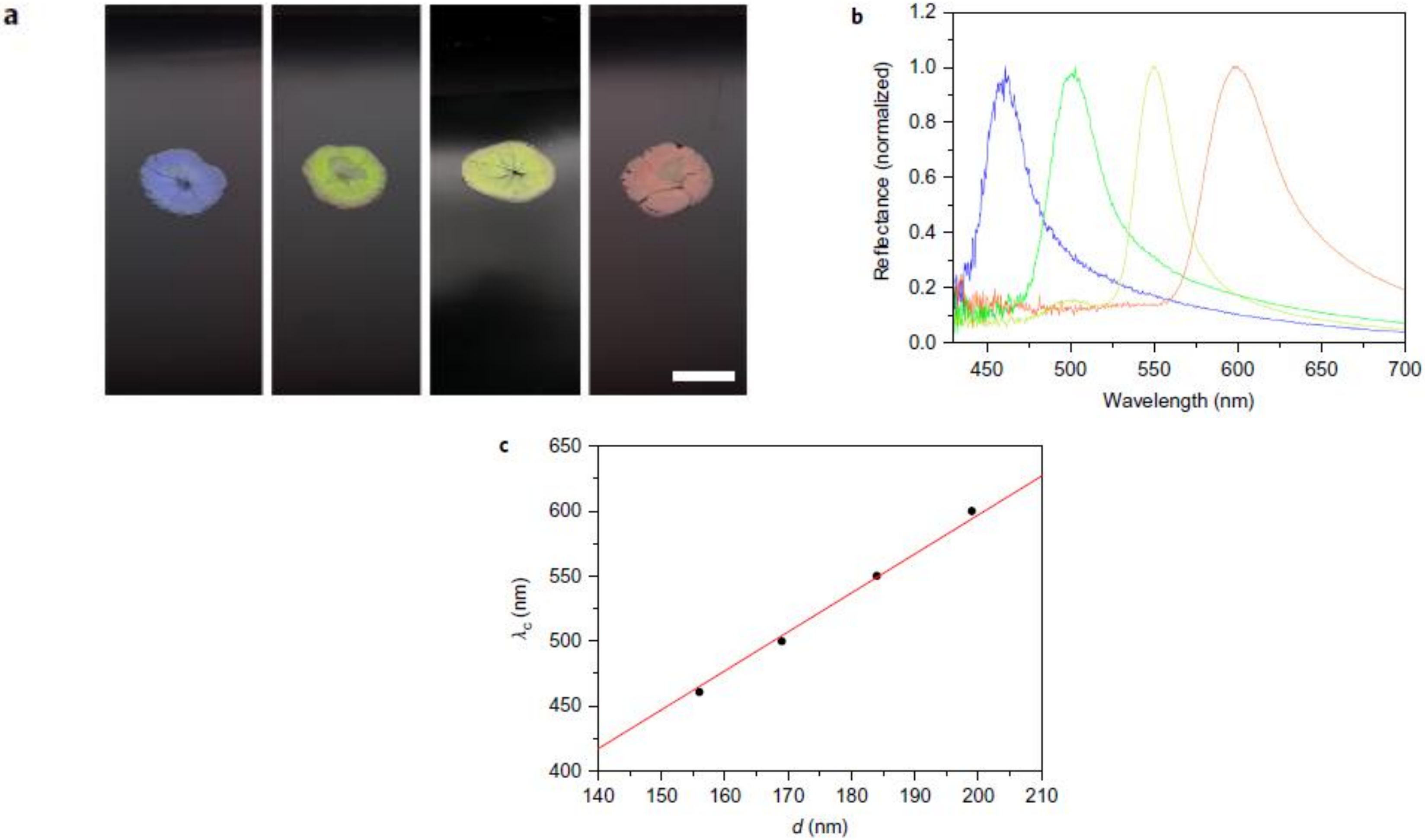


Figure 4 | Photonic properties. a,b, Photographs (a) and normalized optical reflection at θ = 0° of the self-assembled photonic crystals made of TRD ZIF-8 particles of different sizes (b): 178 ± 8 nm (blue); 193 ± 8 nm (green); 210 ± 10 nm (yellow); and 227 ± 10 nm (red). c, Bragg reflection maximum wavelength λ_c plotted against interplanar distance d and fit to the Bragg law (red line) constrained to intercept at zero. Scale bar in a: 1 cm.

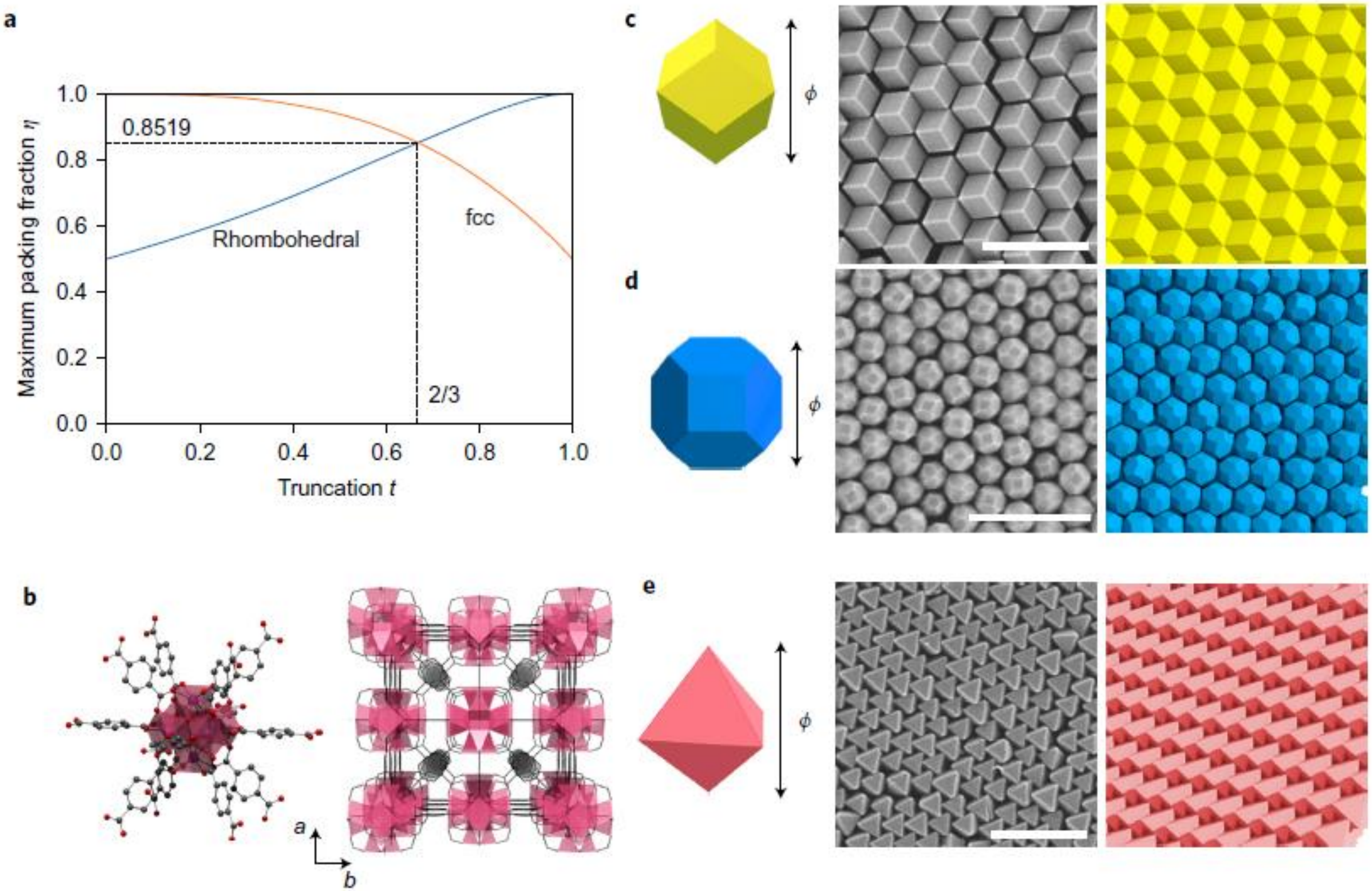


Figure 5 | Ordered self-assembled superstructures made of MOF particles with other morphologies. a, Maximum packing fraction η as a function of truncation t of the ZIF-8 particles for the two possible packing geometries: rhombohedral (blue) and fcc (orange). **b**, Representation of the crystal structure of UiO-66, showing that it is formed by connection of hexanuclear $[Zr_6O_4(OH)_4]$ oxoclusters through 12 terephthalate linkers (atom colour code: Zr, purple; C, grey; O, red). **c–e**, Left: schematic representation of the single MOF particles of the RD ZIF-8 particles (**c**), TRD ZIF-8 particles with t = 0.57 (**d**) and octahedral UiO-66 particles (**e**), respectively. Middle: representative FE-SEM images of the crystals resulting from their respective self-assembly: a plastic fcc crystal (**c**), a regular fcc crystal (**d**) and a hexagonal packing closely related to the Minkowski lattice (**e**). Right: corresponding packings obtained from Floppy-Box Monte Carlo simulations. Scale bars in **c–e**: 1 μm.

Conclusion

- Crystalline, polyhedral TRD ZIF-8 particles can be synthesized with good monodispersity, shape homogeneity and colloidal stability and that self-assembles into millimetre-sized three dimensional ordered arrangements
- Densest rhombohedral packings, are porous and shows a photonic bandgap functionality
- TRD ZIF-8 could be exploited for the use of these materials as responsive materials or sensors
- Can be extended to the formation of ordered arrangements showing different packing geometries to include the self-assembly of crystalline MOF particles with other shapes
- UiO-66 is a promising MOF for catalysis and CO_2 capture due to its large surface area and its high hydrothermal, chemical and thermal stability
- Self-assembled superstructures with long-range periodicities can be used for designing the preparation of materials for applications such as sensing, storage, catalysis and photonics

THANK YOU