

Electronic Supplementary Information

**Modelling critical Casimir force induced self-assembly experiments on patchy colloidal dumbbells**

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**Particle synthesis.** As explained in the main text, the dimer particles are composed of sterically stabilized PMMA spheres with a fluorescently labelled NBD-MAEM core and non-fluorescent shell. The PMMA spheres were synthesized using dispersion polymerization with steric stabilization provided by poly(12-hydroxystearic acid) grafted copolymer (PHS-g-PMMA) following Elsesser *et al.* [1]. Colloidal clusters were fabricated by encapsulating the spherical PMMA particles in toluene droplets in an aqueous phase and selectively evaporating the toluene [2]. To obtain patchy particles, we swell a 0.8%w/w aqueous dispersion of clusters in the presence of 0.1%w/w sodium

dodecyl sulfate with a 10%v/v monomer mixture consisting of 97:2:1 w/w methylmethacrylate : methacrylic acid : ethylene glycol dimethacrylate. We polymerize the swollen particles in an oil bath at 80°C by addition of aqueous potassium persulfate (final concentration in solution: 1.67 mM). The potassium persulfate imparts sulfate charges to the PMMA shell, rendering it hydrophilic with a low surface charge density. The surface of the patch not encapsulated by the PMMA shell is equivalent to that of the PMMA spheres. Therefore, the patches are sterically stabilized by PHS-g-PMMA making them hydrophobic. To separate a synthesized batch into pure dimer, trimer, and higher-symmetry particles, we employ density gradient centrifugation using a sucrose gradient in water. By extracting the 2<sup>nd</sup> and 3<sup>rd</sup> band using a syringe, we obtain a high purity of dimer and trimer particles, respectively. The particles are subsequently suspended in the binary liquid of heavy water and 3-methyl-pyridine (3MP).

Other new methods to fabricate shape shifting patchy particles are given in Refs. [3,4].

## References

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- [4] X. Zheng, M. Liu, M. He, D.J. Pine, and M. Weck, *Angew. Chem. Int. Ed.* **2017**, 56, 5507-5511.