ENTROPIC SELF-ASSEMBLY OF FREELY ROTATING POLYHEDRAL PARTICLES CONFINED TO A FLAT INTERFACE

(SUPPLEMENTARY INFORMATION)

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1 Phase Behavior of TCs

As shown in Fig. S1, as number density increases the system goes from isotropic to square phase via an intermediate tetratic-like phase which is observed for $0.64 < \eta^* < 0.72$ and characterized by ψ_4 and P_4 approximately in the range 0.4-0.8, and 0.3-0.45 respectively. Like in cubes, the intermediate phase forms diffuse $S(\mathbf{k})$ peaks and has liquid like long-range $g(r)$ behavior (see Fig. S2). Also, similar differences ensue for both cubes and TCs in comparing their confined self-assembly in 2D with the bulk self-assembly in 3D[S1].

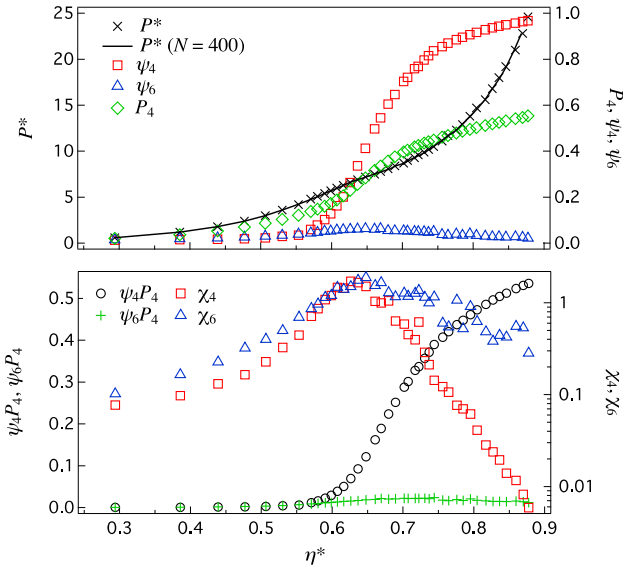

Fig. S1 Equation of state for 1600 TCs obtained by expansion runs. Legend as in Fig. 1 of main text.

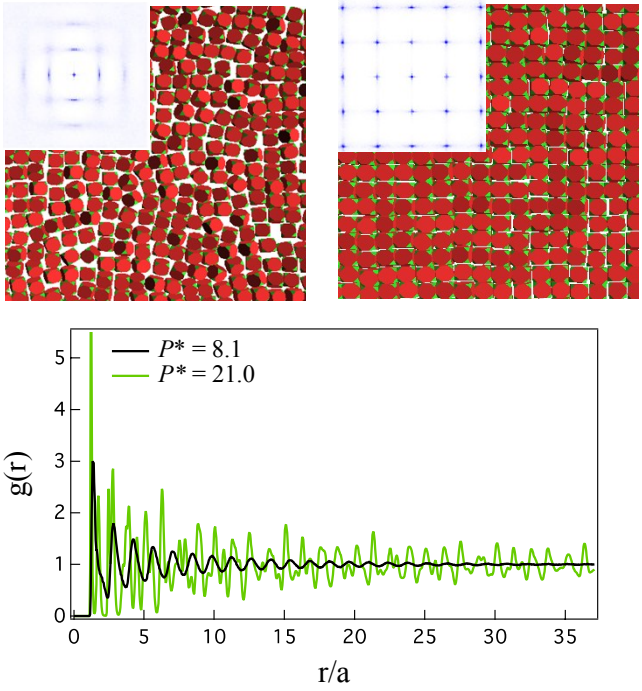

Fig. S2 (Top Panel) Representative snapshots and corresponding structure factors for a system of N=3600 TCs at (left) P^*= 8.1(tetratic-like phase) and (right) P^* = 21.0 (square phase). (Bottom Panel) The radial distribution function for a system of N = 3600 TCs at the same two pressures.

2 Two-Body potentials of mean force (*PMFs*)

The one-dimensional potential of mean force is defined as[S2]

$$\beta PMF(r) = -\ln\left(\left\langle e^{-\beta U(r)}\right\rangle\right) \qquad (1)$$

where $\beta = 1/(k_B T)$ and $U(r)$ is the potential energy of interaction between two particles whose centers of mass are at a distance r. The procedure of calculating $PMF(r)$ involves placing a particle at random position and orientation with center to center distance r from another particle with random orientation. This step is followed by an overlap check using separating axes theorem[S3]. The above procedure is repeated for 10^4 different positions for each value of r and 10^4 combinations of random orientations of the two particles for each position. The fraction of non-overlapping configurations at each value of r corresponds to the average Boltzmann's factors in Eq. (1). Figure S3 shows obtained $PMF(r)$ for different shapes where we set $r = 1$ for the closest distance.

We also obtain the two-dimensional potential of mean force defined as

$$\beta PMF(x,y) = -\ln\left(\left\langle e^{-\beta U(x,y)}\right\rangle\right) \qquad (2)$$

where $U(x,y)$ is the potential energy of interaction between two particles whose centers of mass are at a distance of x and y from each other. These distances are defined relative to a coordinate frame whose origin is the center of mass of a particle with fixed position and orientation, and whose axes are perpendicular to the {100} facets of the fixed particle. For convenience, the fixed particle is oriented in a way that one of the {100} facets of a particle is parallel to the flat interface. The procedure of calculating this $PMF(x,y)$ involves placing a particle at a random orientation with position (x,y) from the fixed particle followed by an overlap check. This step is repeated for 10^4 different orientations for each position. Similar to *PMF(r),* the fraction of non-overlapping configurations at values of (x,y) corresponds to the average Boltzmann's factors in Eq. (2). Figure S4 shows the contour plots of $PMF(x,y)$ where for each shape we make the x and y distances dimensionless by dividing their values by the closest distance [which was obtained from $PMF(r)$ and corresponds to the particle indiameter σ_{in}].

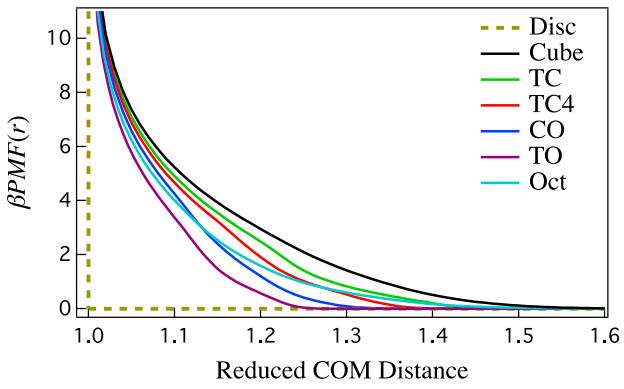

Fig. S3 One-dimensional potential of mean force, $PMF(r)$ for different shapes studied in this work.

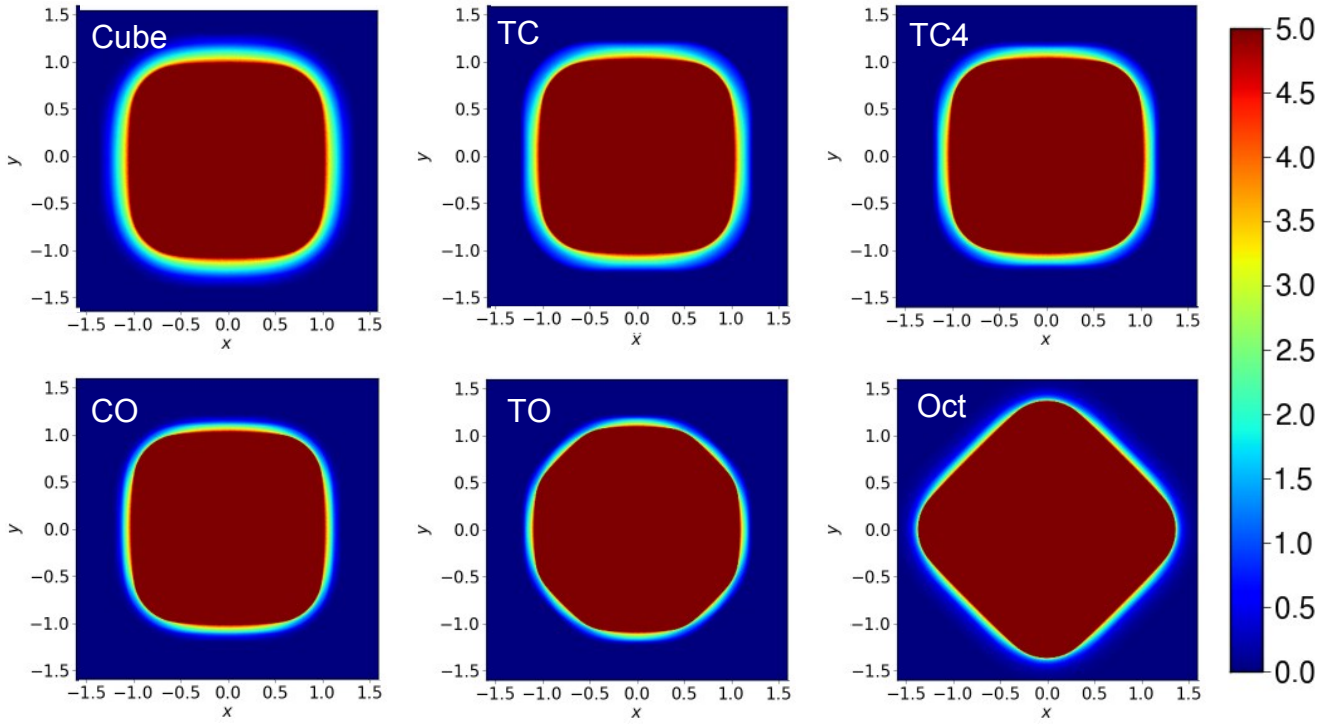

Fig. S4 Two-dimensional potential of mean force, $PMF(x,y)$ for different shapes studied in this work. The colorbar varies from $\beta PMF(x,y) = 0$ to 5. The values of $\beta PMF(x,y) > 5$ are labeled as red.

3 Adsorption Energy

We apply a model used in Refs. S4 and S5 to estimate the adsorption energy of a single particle on a fluid-fluid flat interface. The adsorption energy, F of a truncated cube as a function of its position and orientation is given by

$$F(z,\delta,\omega) = \gamma_{tb}(A - S_{tb}) + \gamma_{1t}S_{1t} + \gamma_{2t}S_{2t} + \gamma_{1b}S_{1b} + \gamma_{2b}S_{2b} + \text{const.} \qquad (3)$$

Here, γ_{tb} is the interfacial tension between the top and bottom fluid, A is the total surface area of the interface and S_{tb} is the interfacial area excluded due to the presence of a particle. The surface tension between particle's facets of type i (i = 1,2 for {100} and {111} facets respectively) and top fluid is denoted by γ_{it} and the surface tension between particle facets of type i and bottom fluid is denoted by γ_{ib}. The surface areas of facets of type i in the bottom and top medium are denoted by S_{it} and S_{ib} respectively. The value of the arbitrary additive constant is chosen such that $F = 0$ when a particle is completely immersed in the bottom fluid. The position or immersion depth of a particle, z, is the height of its center of mass relative to an interface, which is parallel to the xy plane with its normal pointing in the z-axis direction and positioned at $z = 0$. The orientation of a truncated cube is given by two angles: the polar angle δ and the azimuthal angle ω. As shown in Ref. S4, using the Young's equation, Eq. 3 is simplified to

$$F(z,\delta,\beta) = \gamma_{tb}(\cos\theta_1 S_{1t} + \cos\theta_2 S_{2t} - S_{12}) \qquad (4)$$

where θ_i is the contact angle corresponding to the three-phase contact between facet of type i, top fluid and bottom fluid. To obtain F for (experimentally relevant) contact angle values of θ_1 and θ_2 for any given (z, δ, ω), the surface areas S_{it}, S_{ib} and S_{tb} are estimated using the triangular tessellation technique described in Ref. S6. The three dimensional landscape of adsorption/interfacial energy is then obtained by repeating the procedure for all possible orientations and positions, where we vary, z within ($-H$,H)

where H is a value slightly larger than the circumradius of a shape (for TC4 we use H as the largest circumscribing radius), δ from $[0,\pi/2]$, and ω from $[0,\pi/4]$ using 100 equidistant steps for each of these three parameters. Due to the symmetry properties of a truncated cube, the polar angle and azimuthal angle are varied up to $\pi/2$ and $\pi/4$ respectively. The most stable configuration is then obtained by estimating the global minimum of this landscape and the value of F corresponding to the global minimum is denoted as $F_{minglob}$. The model also provides the interfacial energy, $F_{min}(z)$ of a particle as a function of z minimized with respect to angles δ and ω. The estimation of $F_{min}(z)$ at different values of z is performed for a cube shaped particle of size 3 nm adsorbing on a toluene-air interface at room temperature. The value of interfacial tension, γ_{tb} is given by 28.52 mN/m (room temperature). The profile of $F_{min}(z)$ versus z is shown for different contact angles ranging from $\cos\theta_1 = 0.0$ to $\cos\theta_1 = 0.5$ in Fig. S5.

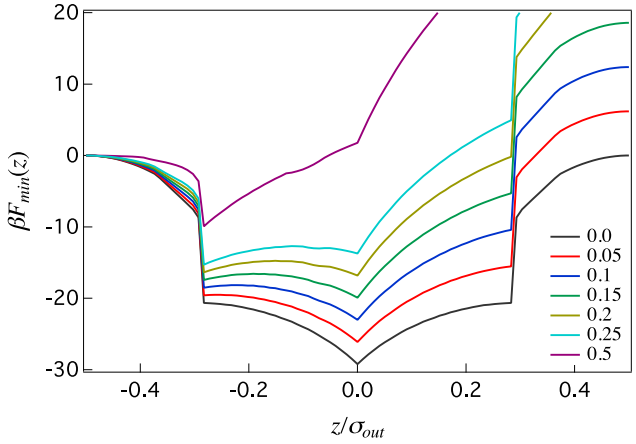

Fig. S5 The profile of $F_{min}(z)$ versus z for a cube shaped particle for different contact angles ranging from $\cos\theta_1 = 0.0$ to $\cos\theta_1 = 0.5$ (as per numbers in the inside legend) .

For $\cos\theta_1 = 0.0$ and $\cos\theta_2 = 0.0$, we show the difference $\Delta F_{orient}(\delta, \omega) = F(z_{opt}, \delta, \omega) - F_{minglob}$ as a function δ and ω for different shapes in Fig. S6, where the value, z_{opt} is the immersion depth of the most stable configuration. For the plots shown in Fig. S6, the cube size is 3 nm whereas the size of the other shapes is selected to have the same surface area as that of the 3 nm cube. For each shape, we also show in Fig. 6 snapshots of three different configurations whose $\Delta F_{orient} <= 5k_BT$. We also obtain the percentage of angular phase space, P_{orient}, that has $\Delta F_{orient} <= 5k_BT$; this is estimated by evaluating ΔF_{orient} over a grid of (δ, ω) pairs and finding the fraction for which $\Delta F_{orient} <= 5k_BT$.

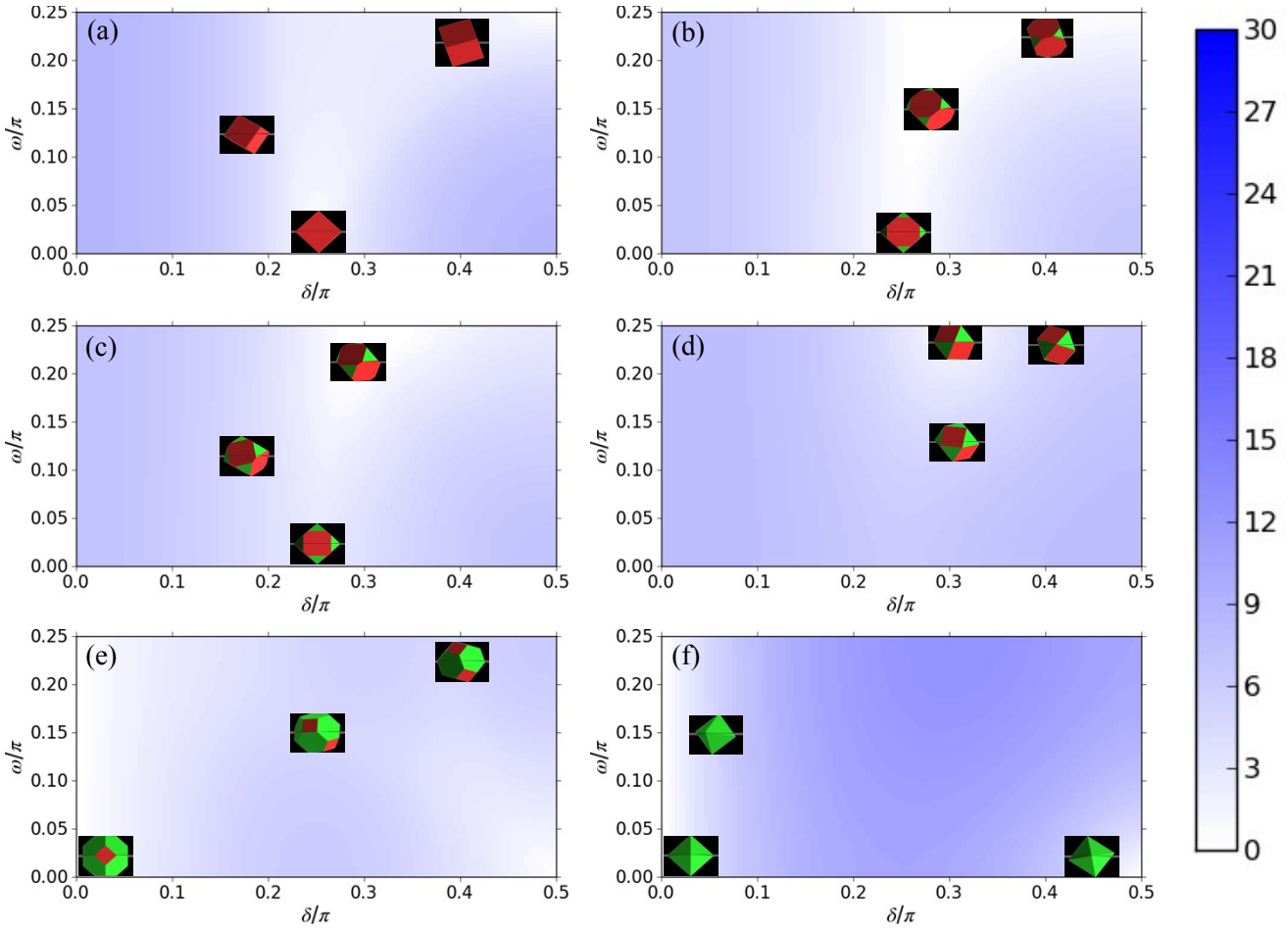

Fig. S6 The energy difference, ΔF_{orient} as a function of δ and ω for (a) cube, (b) TC, (c) TC4, (d) CO, (e) TO and (f) Oct at contact angle values of $\theta_1 = 90$ degrees and $\theta_2 = 90$ degrees. The snapshots of configurations at three different (δ, ω) values with $\Delta F_{orient} <= 5k_BT$ are also shown for each shape (the interface plane, perpendicular to the plane of the page, appears as a horizontal line, and for the particles the {100} facets are colored red and the {111} facets are green).

References:

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S6. J. de Graaf, M. Dijkstra, and R. van Roij, *J. Chem. Phys.* **132**, 164902 (2010).