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Abstract: A new type of armored droplets, so-called polyhedral liquid marbles are introduced in this work. These armored liquid marbles consist of liquid droplets stabilized by hydrophobic hexagonal plates made of poly(ethylene terephthalate), which adsorb to the liquid-air interface. Depending on the specific combination of plate size and droplet diameter, the plates self-assemble into highly ordered hexagonally arranged domains. Even tetrahedral-, pentahedral-, and cube-shaped liquid marbles composed of only 4 to 6 plates are demonstrated. During evaporation of the internal liquid, due to the high adsorption energy of the plates at the liquid-air interface, the overall surface area stayed constant resulting in strongly deformed polyhedral liquid marbles. In line with this, highly asymmetric polyhedral liquid marbles and letters are obtained due to the strong interfacial jamming exerted by the rigid hexagonal plates. This is particularly pronounced for larger plate sizes leading to liquid marbles with unusually sharp edges (for example, rectangular edges). The polyhedral liquid marbles exhibit various stimuli-responsive behaviors simultaneously being exposed to water,

ammonia or tetrahydrofuran vapors. Air-driven polyhedral liquid marbles floating on water can reach velocities of several cm per second.

Studying the adsorption of solid particles at air-water and oil-water interfaces is of broad interest^[1] and has led to novel concepts and materials such as ‘colloidosomes’,^[2] ‘armored bubbles’,^[3] ‘dry water’,^[4] and ‘liquid marbles (LMs)’.^[5] LMs are liquid droplets stabilized by solid particles adsorbed at the liquid-gas interface, which behave as non-wetting soft, elastic objects. The particles shield the inner liquid from wetting the underlying substrate. In contrast to emulsions and foams, which can be stabilized by solid particles *and* molecular surfactants, LMs in air require particles and cannot be stabilized by molecular surfactants. Recently, LMs have attracted considerable attention in view of their potential applications in transport and microfluidics,^[6] miniature reactors,^[7] microcapsules,^[8] personal and health care products,^[9] sensors,^[10] accelerometers,^[11] and pressure-sensitive adhesives^[12] because of their ability to encapsulate functional materials.

LMs can be prepared using solid particles with various chemical compositions including organic, inorganic and composite particles. Most of the literature is concerned with (near) spherical particles and their flocs. However, there are no studies on LMs stabilized with well-defined non-spherical particles or stabilizers. Thus, it is crucial to reveal and understand the relationship between solid particle shape and LM structure formation to utilize the LMs.

Herein, we introduce a new type of LMs, so-called polyhedral LMs. The polyhedral LMs are stabilized using hydrophobic hexagonal plates monodisperse in shape and size. The questions addressed in this study are: (1) Can hexagonal plates stabilize LMs? Which ratio between plate and drop size can be achieved? (2) How do the plates self-assemble at a curved air-water interface, especially when the curvature and plate size are comparable? (3) What are the properties and functionalities of the polyhedral LMs?

Poly(ethylene terephthalate) (PET) hexagonal plates (**Figure 1a**) with monomodal distributions in both size (Major axis: $A = 2s = 0.27 \pm 0.04$ mm (15% rel. error), 0.34 ± 0.01 mm (3% rel. error), 1.14 ± 0.04 mm (4% rel. error) and 2.48 ± 0.04 mm (2% rel. error); side length $s = 0.14$ mm, 0.17 mm, 0.57 mm and 1.24 mm, respectively) and thickness ($d = 40\text{--}55$ μm for all the samples) were used in this study (Figure S1 for optical and scanning electron microscopic (SEM) images). The original PET plates were hydrophilic and wetted by water, being unable to stabilize LMs. The plates were hydrophobized by modification with 1H,1H,2H,2H-perfluorodecyltrichlorosilane in *n*-hexane. X-ray photoelectron spectroscopy confirmed the surface coating of the PET plates by the silane (Figure S2). The static contact angle of a 10 μL water droplet measured on a fluorinated PET sheet was $110^\circ \pm 5^\circ$ (critical surface tension was determined to be approximately 6 ± 2 mN m^{-1} by Zisman plot; Figure S3) indicating a hydrophobic fluorinated surface.

Water droplets (60 μL) were deposited onto the dried hydrophobic plates using a micropipette. During gentle rolling of the water droplets on the beds, the liquid was spontaneously encapsulated by the plates and LMs were formed (Figure 1b). The coating of the water droplets by the plates rendered them both, hydrophobic and non-wetting. The plates adsorbed at the air-water interface of the droplet form a certain contact angle θ with respect to the side wall of the plates (Figure 1c,d) which is mainly determined by the hydrophobic surface modification of the plates. Imaging of the lower side of a polyhedral LM using laser scanning confocal microscopy (LSCM) revealed that the contact line is pinned at the inner edge of the plates, roughly in parallel with the plate's long surface and perpendicular to its normal direction ($\theta \approx 90^\circ$). The air-water interface and thus the droplet (Figure 1d, bottom; shown in blue) was trapped at the inner side of the plates. In accordance with that, the distance h between the outer side of the plates (Figure 1d, bottom, reflection on the outer side

of the plate shown in yellow) and the air-water interface was $\approx 40\text{ }\mu\text{m}$ which corresponds to the thickness of the plates. This resembles the situation of a water droplet on a superhydrophobic surface consisting of fluorinated micro pillars.^[13, 14] Hence, the hexagonal plates act as a mobile micropillar layer. The LMs remained stable even after transfer from the plate beds onto solid substrates, such as PET or hydrophilic glass slides.

Optical microscopy images show the microstructure of the LMs prepared using 0.27 mm, 0.34 mm, 1.14 mm, and 2.48 mm-sized plates, placed on a hydrophilic glass slide (Figure 1e, left to right). Polyhedral LMs were formed in all cases. Plates spontaneously arranged in a hexagonal two-dimensional crystal-like structure, which is readily apparent on the LM surfaces of the 0.34 and 1.14 mm-sized plate systems (Figure 1f). If the droplet diameter (here: $D \approx 6\text{ mm}$) is much larger than the plate size, the droplet curvature is low and the plates can fully attach in a parallel orientation and form well-ordered two-dimensional domains, resulting in a crystal phase on the curved surface. This was mainly observed for the monodisperse 0.34 mm-sized plates. The plates spontaneously self-assembled to form well-ordered arrays on the drop's surface just by rolling, even though the LMs were formed from randomly oriented plate beds.

Figure 1. a) Schematic of the hexagonal fluorinated PET plates used to stabilize polyhedral liquid marbles (LMs) with thickness d , main axis A , and side length s . b) Schematic of a polyhedral LM. c) Optical microscopic images of plates (yellowish; with $A = 2.48$ mm) adsorbed on a 60 μL water droplet (with Brilliant Blue dye, 20 mg L^{-1}). Scale bar: 500 μm . d)

The fluorinated plates adsorb to the air-water interface forming a contact angle θ . Laser scanning confocal microscopy (LSCM) image from underneath a polyhedral LM (15 μL water containing ATTO488, fluorescence shown in blue, reflections in yellow) shows that $\theta \approx 90^\circ$. The distance h between the outer side of the plate and the air-water interface is $\approx 40 \mu\text{m}$. e) Optical microscopy images of polyhedral LMs prepared with different plate sizes ($A = 0.27 \text{ mm}$, 0.34 mm , 1.14 mm , and 2.48 mm ; left to right) and different droplet volumes ($60 \mu\text{L}$, $30 \mu\text{L}$, and $15 \mu\text{L}$; top to bottom). Scale bar: 1 mm . f) Magnified microscopic images revealing the microstructure of the polyhedral LMs with different plate sizes ($A = 0.27 \text{ mm}$, 0.34 mm , 1.14 mm , and 2.48 mm ; left to right). Scale bars: $500 \mu\text{m}$. g) By tuning the plate to water ratio ($15 \mu\text{L}$ droplets with brilliant blue dye) using the largest 2.48 mm -sized plates (a total of 4 to 6 plates from left to right), different polyhedral morphologies were obtained. Scale bar: 1 mm . h) SEM image of a dried cyanoacrylate-treated $3 \mu\text{L}$ polyhedral LM using 0.34 mm -sized plates. Scale bar: $200 \mu\text{m}$.

Parts of the plates stuck out of the LM's surface into the air phase in case of the largest 2.48 mm -sized plate system, where the droplet diameter ($D \approx 6 \text{ mm}$) was comparable to the plate size. The plates were tangent to the LM surface. A significantly lower degree of order was observed for the smallest 0.27 mm -sized plate system correlating to its higher polydispersity in size.^[15] Additionally, smaller particles can lead to less ordered structures.^[16]

Diameters of the LMs were varied in a range between approximately 5.7 mm and 2.5 mm simply by changing the volume of the inner water droplet ($60 \mu\text{L}$ – $15 \mu\text{L}$) (Figure 1e; top to bottom). For the 0.27 and 0.34 mm -sized plate systems, the decrease of droplet volume yielded more spherical LMs. Since the plate sizes were much smaller than the radii of the droplets, the plates could fully attach to the droplets' surfaces. The 1.14 mm -sized plates started to stick out of the LM's surfaces into the air phase for droplet volumes $\leq 30 \mu\text{L}$. The

droplet curvature increased, and the stiff plates could only partially attach to the droplet surface. Using the 2.48 mm-sized plates, polyhedral LMs with near-spherical shape formed for 30 μL droplets. Notably, when reducing the drop volume to 15 μL droplets ($D \approx 2.5$ mm), LMs with various polyhedral shapes, including tetrahedron, pentahedron, and cube were obtained by tuning the plate to water ratio (Figure 1g). Depending on the amount of plates adsorbed on the water drop, the polyhedral LM spontaneously assumed the different shapes. Water drops could be stabilized using as few as 4 to 6 plates. To the best of our knowledge, this is the lowest number of plates that has ever been used to stabilize a water drop. Due to the shape and rigidity of the hexagonal plates, the droplet could not be fully covered by the plates, leading to LMs with open faces. This is especially apparent for the polyhedral LM with 5 plates (Figure 1g; middle). Here, the hexagonal plate on the top and bottom of the LM kept the axial plates apart, whereas the capillary forces kept them in place, yielding a very uniquely shaped LM.

Large LMs using 0.34 mm and 2.48 mm-sized plates containing 120, 480, and 960 μL water droplets were fabricated. Their shapes changed from oblong to puddle with an increase of droplet volume (Figure S4). Crystalline two-dimensional array structures developed in large areas. Despite the difference in nature of the materials and length scales, the patterns formed on the LM surfaces are similar to the honeycomb structure built by honey bees in their nests. For the large plates, the size of the crystalline domains continually increased as the droplet/plate size ratio became larger. On the other hand, using the smaller 0.34 mm-sized plates, crystalline domain sizes hardly changed for drop volumes of 480 μL and 960 μL . Up to 50 plates per two-dimensional crystal were observed, corresponding to domain sizes of approximately 3–4 mm.

The liquid-air interface of a 3 μL polyhedral LMs was solidified by exposing it to ethyl 2-cyanoacrylate vapor, the main component of superglues. Ethyl 2-cyanoacrylate readily absorbs and polymerizes at air-water interfaces,^[17] solidifying the water interface between and underneath the plates. After superglue treatment, the polyhedral LM preserved its spherical polyhedral morphology and did not collapse during/after the drying process, indicating that the surface of these LMs was rigid (Figure 1h). The hexagonally-packed plate arrays were mostly preserved. Detailed SEM images show that only a monolayer of the hexagonal plates was adsorbed at the air-water interface and confirm $\theta \approx 90^\circ$ obtained by the LSCM images (Figure S5).

Figure 2. a,b) Microscopic images from the top (a) and side view (b) showing morphological changes of polyhedral LMs (15 μL ; 0.34 mm-sized plates) during evaporation. Scale bars:

500 μm . c) Comparison of the evaporation of a polyhedral LM (15 μL ; 0.34 mm-sized plates) at $36\pm5\%$ relative humidity (RH) versus a 15 μL water droplet on a superhydrophobic substrate (average of three repeats at an avg. RH of $37\pm5\%$) at $21\text{--}22\text{ }^{\circ}\text{C}$. d) Weight loss during evaporation of polyhedral LMs (15 μL ; 0.34 mm-sized plates) at different humidities ($56\pm5\%$ RH, $45\pm5\%$ RH, and $36\pm5\%$ RH).

When drying the polyhedral LMs, the morphology changed. As an example, drying of a polyhedral LM of 15 μL volume armored with 0.34 mm-sized plates is shown in **Figure 2a,b** (Figure S6 for examples of the 0.27 mm and 1.11-mm sized plate systems). Slow evaporation of the inner water of the LM induced buckling on the LM's surface. This can be explained by the surface jamming effect of the plates at the air-water interface due to the high adsorption energy ΔG at the interface. The adsorption energy (ΔG) is defined as the difference in free energy between a system where one face of a plate is in contact with water as compared to a system where the plate is fully in contact with air plus a free air-water interface. Thus, ΔG can be estimated using Eq. 1 (see Supporting Information for details).

$$\Delta G = \frac{3\sqrt{3}}{2} s^2 (\gamma_{AS} + \gamma_{AW} - \gamma_{WS}) \quad (\text{Eq. 1})$$

where $\gamma_{AS} = 6\text{ mN m}^{-1}$, $\gamma_{WS} = 30\text{ mN m}^{-1}$, and $\gamma_{AW} = 72\text{ mN m}^{-1}$ are the air-plate, water-plate, and air-water interfacial energies, respectively (γ_{WS} was determined using Young's equation with a water contact angle of 110°). Using Eq. (1), the ΔG values of the plates at air-water interfaces were calculated to be $2\times 10^{-9}\text{ J}$, $4\times 10^{-9}\text{ J}$, $4\times 10^{-8}\text{ J}$, and $2\times 10^{-7}\text{ J}$ for 0.27 mm, 0.34 mm, 1.14 mm, and 2.48 mm-sized plates, respectively. These values are more than three orders of magnitude higher than those of micrometer-sized spherical particles adsorbed at the air-water and oil-water interfaces.^[18]

The plates did not detach or flip off during evaporation, because of the high adsorption energy. The total surface area of the LM stayed almost constant and it adjusted its surface-to-volume ratio by deformation. For comparison, a bare water droplet placed on superhydrophobic substrate decreased its volume via evaporation while keeping a near-spherical shape (Figure S7). In contrast to the LM, the air-water interfacial area decreased along with the decrease of droplet volume.

The water evaporation of the LMs and bare water droplets (Figure 2c,d) was evaluated gravimetrically at 21–22 °C and three humidities varying between 35% and 55% relative humidity (RH). Surprisingly, the mass and thus volume decreased almost linearly with time for the LMs. The water evaporation rate of a polyhedral LM of 15 μL volume was $\approx 0.14 \text{ mg min}^{-1}$ and the water was completely evaporated after $\approx 105 \text{ min}$ at $36 \pm 5\% \text{ RH}$. At $45 \pm 5\%$ and $56 \pm 5\% \text{ RH}$ the evaporation of the inner liquid slowed down and evaporation times increased to $\approx 125 \text{ min}$ and $\approx 155 \text{ min}$, respectively. The evaporation of bare water drops of the same volume followed the $V^{2/3}$ law,^[19] implying that evaporation is determined by the shrinking spherical shape of the drop (Figure S8). At 21–22 °C and avg. RH of $37 \pm 5\%$ the droplet was evaporated after $\approx 110 \text{ min}$. Thus, even though the polyhedral LM was armored with hexagonal plates, the evaporation of the inner liquid was slightly faster than that a bare spherical droplet due to the fact that the LM retained its surface areas whereas the bare droplet decreased its surface area.^[20] The final stage of drying is interesting: the LMs broke down due to gravity and left cohesionless residues of plates after complete drying. Just before complete evaporation, the plates stuck to each other due to lateral capillary forces mediated by residual water.

Figure 3. a) Spherocylindrical jammed polyhedral marble with aspect ratio of 12 prepared with 0.34 mm-sized plates. Scale bars: 5 mm (left), 2 mm (right). b) Polyhedral letter “L” by deforming the high aspect ratio LM. Scale bar: 5 mm. c) Dumbbell-like shaped polyhedral LM with convex and concave areas. Scale bar: 5 mm. d) Polyhedral letter “A” showing strong interfacial jamming and shape control, formed with 2.48 mm-sized plates. Scale bar: 5 mm. e) Initials of the term polyhedral liquid marble: PHLM, formed using transparent 2.35 mm-sized plates and dyed water. The edges of the letters can be very sharp (see inset of letter “L”). Scale bar: 5 mm, 500 μm (inset). f) The edge angle δ of the polyhedral LMs can be tuned between $>120^\circ$ and $<45^\circ$. Scale bar: 500 μm . g) Merging of two polyhedral LMs having a blue and a pink dye to form the letter “Q”. The mixing of the two dyes can be observed inside of the resulting LM. Scale bar: 5 mm.

Spherocylindrical polyhedral LMs (**Figure 3a**) with aspect ratios larger than 10 can be created by (1) merging polyhedral LMs, by (2) withdrawing liquid from the marble and by (3) placing excess plates on prepared LMs and deforming those by external forces. To obtain cylindrical marbles, we rolled the LMs back and forth along one axis. Being able to make cylindrical LMs is strikingly different from bare droplets, where the surface area is minimized in order to minimize the interfacial energy. The LMs behaved in an inelastic manner and the long cylindrical shapes did not undergo a Rayleigh-Plateau capillary instability. The inelastic characteristics arise from steric jamming of plates at the air-water interface. Jamming of colloidal particles at interfaces has already been employed to kinetically trap fluid morphologies, including non-spherical armored bubbles and droplets^[21] as well as bicontinuous interfacially jammed emulsion gels (bijels).^[22]

The shapes of the jammed LMs can be plastically rearranged to various stable configurations if subject to inhomogeneous external stresses (Figure 3b,c). The high aspect ratio cylindrical LM could be rearranged to write the letter “L” (Figure 3a to Figure 3b) by applying an external force using a spatula. Additionally, a dumbbell-like shape could be obtained (Figure 3c). We found that the large plates exhibit an even stronger interfacial jamming. Deposition and rolling of water drops on the plates already yielded highly deformable polyhedral LMs. Thus, the liquid letter “A” was easily formed using the 2.48 mm-sized plates (Figure 3d). This principle was expanded to transparent $A = 2.35 \pm 0.03$ mm-sized plates (Figure S9). By merging a few LMs, the initials of polyhedral liquid marble “PHLM” were written (Figure 3e, Movie S1 shows the strong interfacial jamming behavior and formation of letters within a few seconds). It should be noted that these LMs can feature extremely sharp edges having an angle of 90° (see inset in Figure 3e). We tuned the edge angles δ of a polyhedral LM between $>120^\circ$ and $<45^\circ$ (Figure 3f). Such well-defined edges were previously not available with common LMs prepared using spherical particles or particle aggregates. By merging two LMs

containing different dyes (pink and blue dye), the letter “Q” was formed. The merging of the dyes inside of the resultant LM could be observed through the transparent PET plates, indicating that the liquid phases became continuous.

There are four criteria which must be satisfied to realize these inelastic shape-controlled LMs: (1) The plates need to be hydrophobic and show an advancing contact angle of $>90^\circ$, (2) the adsorption energy of the plates at the air-water interface must be large enough to prevent desorption, (3) the rate of formation of LMs and assembly of the plates must be fast compared to relaxation of the water droplets, and (4) the plate-coated film formed at the LM surfaces must be robust enough to maintain the integrity of the structured liquids.

To show that the jammed interface is not a thermodynamically stable state, we exposed a cylindrical polyhedral LM containing hygroscopic saturated LiCl solution to water vapor (Figure S10a). The cylindrical shape gradually changed to a spherical shape during water uptake from the vapor phase (due to an increase of droplet volume and surface area), indicating relaxation of the jammed interface. The polyhedral LM grown via water absorption was now placed under dry atmosphere in the presence of silica gel (Figure S10b). The LM size decreased, keeping its spherical shape and eventually started buckling. After 50 h the LM was dried. This dried polyhedral LM was now exposed to humid atmosphere again, leading to growth of the LM. It resumed to its previous spherical shape (Figure S10c), yet the LM could not return to its non-equilibrium jammed cylindrical shape. This further demonstrates that the jamming can be released by an external stimulus.

Figure 4. a,b) Schematic of a stimuli-responsive polyhedral LM. Due to the absorption of (a) NH_3 vapor and the resulting pH changes, the LM (containing phenolphthalein) changes its color from colorless and transparent to violet. The absorption of (b) tetrahydrofuran (THF) leads to a decrease of surface tension of the inner liquid and thus a Cassie-to-Wenzel-like transition between the hexagonal plates. c) Stimuli-responsive polyhedral LM (30 μL , 1.13 mm-sized transparent plates) exposed to NH_3 vapor for 120 s, and subsequently to THF vapor. Scale bar: 2 mm. d) A polyhedral LM (15 μL ; 0.34 mm-sized plates) floating on a planar water surface. The two air-water interfaces are separated by just a monolayer of plates which corresponds to a distance of $h \approx d \approx 40 \mu\text{m}$. Scale bar: 0.5 mm. e) Locomotion of a 15 μL

polyhedral LM on a water surface driven by air blows. f,g) Path and corresponding velocity analysis of air-driven polyhedral LM locomotion on water for 2 blows. h) Stimuli-induced disruption of a 15 μL polyhedral LM by addition of THF to the water surface. The LM contained a 3 wt% NaOH solution and the water reservoir contained phenolphthalein dye. Scale bar: 0.5 mm.

Polyhedral LMs are simultaneously responsive to different stimuli (**Figure 4a,b**). A transparent polyhedral LM (prepared with $A = 1.13 \pm 0.04$ mm-sized transparent PET plates) containing 30 μL water with the pH-responsive dye phenolphthalein was first exposed to ammonia vapor (Figure 4c). The absorption of ammonia increases the pH from neutral to slightly basic resulting in a color change of the liquid inside of the LM at pH = 8.2. Close observation of the LM (Figure S11) shows that the ammonia vapor penetrated through the gaps between the PET plates and slowly diffused and distributed over the whole liquid marble. After complete color change, the LM was exposed to tetrahydrofuran (THF) vapor. Within the first 30 s of exposure, the volume of the LM increased slightly. Then, suddenly after 33 s, the polyhedral LM collapsed. Due to uptake of THF, the surface tension of the liquid phase inside of the LM decreased. At a certain point, the liquid started wetting the plates, most likely inducing a Cassie-to-Wenzel-like^[13] transition. The liquid started contacting and spreading on the glass slide underneath. A photograph, captured from underneath a broken LM (Figure S12) prepared with non-transparent plates and exposed to THF, shows that the liquid spread towards a certain direction (here: towards the left).

Surprisingly, although polyhedral LMs exhibit only one monolayer of plates, they can be transferred and float on a planar water surface (Figure 4d). After transfer, the liquid-air interfaces of the water inside and underneath the LM are separated by just one monolayer of

plates (Figure S13). The polyhedral LM remained stable on the water surface and could float for more than 1 h. The distance between the two interfaces h should be close to the plate thickness $d \approx 40 \text{ }\mu\text{m}$. Nonetheless, this tiny air gap is enough to separate the two water interfaces and let the polyhedral LM float. Fast locomotion of the LM on water can be induced by air blowing (Figure 4e). Depending on the strength of the blow, the LMs traveled several cm and reached peak velocities of almost 10 cm s^{-1} . This results in accelerations of up to 60 cm s^{-2} and forces of up to $10 \text{ }\mu\text{N}$ (Figure 4f,g). A floating LM was disrupted by addition of THF to the water surface (Figure 4h, Movie S2 shows the locomotion of a polyhedral LM induced by air blowing and disruption via THF). The LM contained $15 \text{ }\mu\text{L}$ of a highly basic 3 wt% sodium hydroxide solution. After disruption, the LM changed the pH and color of the underlying water reservoir, which contained phenolphthalein. Thus, the LMs may be used as pH and surface tension sensitive sensors.

In conclusion, LMs stabilized by hydrophobic hexagonal PET plates are introduced. The arrangement of the plates depends on the ratio of the plate diameter A and the drop diameter of D . For small drops, where D and A are of the same order of magnitude, the self-assembly of the hexagonal plates on the surface of the LMs results in the first examples of uniquely shaped polyhedral LMs including cubic, tetrahedral and pentahedral structures. A similar yet different phenomenon is known from the so-called capillary origami where a highly elastic sheet wraps a droplet.^[23] In contrast, the PET plates are rigid and not bend by the capillary forces. For large drops ($D \gg A$), the surfaces of the LMs are composed of two-dimensional polycrystalline arrays of plates. The high adsorption energy of the plates at the air-water interface of the LMs prevents the plates from detaching, e.g. during evaporation, and leads to interfacial jamming. Highly jammed non-equilibrium shaped LMs such as cylindrical drops and letter-shaped marbles can be formed. Those LMs exhibit tunable and extraordinarily

sharp edges. The polyhedral LMs are stable enough to move on planar water surfaces and can be used as sensors as they are responsive to different stimuli simultaneously. The use of the hexagonal plates enables unprecedented shape control and the methodology for generation of these crystalline structures on curved surfaces is simple, scalable, and based on sustainable materials.

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A new type of liquid marbles, so-called polyhedral liquid marbles are introduced. These armored spheres consist of liquid droplets stabilized by hydrophobic hexagonal plates, absorbing to the liquid-air-interface. Various intriguing forms and shapes, exhibiting highly ordered crystalline plate arrays are demonstrated. The polyhedral liquid marbles show strong interfacial jamming and are stimuli-responsive.

Liquid Marbles

Florian Geyer, Yuta Asaumi, Doris Vollmer, Hans-Jürgen Butt, Yoshinobu Nakamura, and Syuji Fujii*

Polyhedral Liquid Marbles

Supporting Information

Polyhedral Liquid Marbles

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*Experimental section**Materials:*

Experiments were carried out at room temperature. The following chemicals were used: 1*H*,1*H*,2*H*,2*H*-perfluorodecyl-trichlorosilane (96%, TCI), *n*-hexane (96%, Wako), ethanol (95%, Sigma-Aldrich), isopropanol (SAJ first grade, Sigma-Aldrich), tetrahydrofuran (SAJ first grade, Sigma-Aldrich), ammonia solution (28%, Sigma-Aldrich), lithium chloride (99.0%, Wako), sodium hydroxide ($\geq 97\%$, Sigma-Aldrich), ethyl 2-cyanoacrylate (Aron Alpha Extra Sokkotayoto, Toagosei Co., Ltd.), Brilliant Blue (San-Ei Gen F.F.I., Inc.), Food Red No. 106 (San-Ei Gen F.F.I., Inc.), phenolphthalein (extra pure, Kanto Chemical Co., Inc.), ATTO488 (ATTO-TEC). Purified and deionized water from Advantec MFS RFD240NA (GA25A-0715) was used for all experiments. Hydrophilic PET plates ($A = 0.34 \pm 0.01$ mm (3% rel. error)) were purchased from Matsumura Kogei Co., Ltd. The other hydrophilic PET plates ($A = 0.27 \pm 0.04$ mm (15% rel. error), 1.14 ± 0.04 mm (4% rel. error) and 2.48 ± 0.04 mm) were purchased from Matsuno Industry Co., Ltd. Transparent hydrophilic PET plates ($A = 1.13 \pm 0.04$ mm and 2.35 ± 0.03 mm) were obtained from Nakajima Metal Leaf, Powder Co. Ltd. Reagents were used as received.

Hydrophobization of the plates:

The pristine plates (5–10 g) were washed repeatedly with ethanol (200–400 mL) until the supernatant remained clear (3–7 repeats). The washed plates were dried in vacuum overnight. Afterwards, the dried plates were modified with 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane (PFDTs). Therefore, 3–10 g of the plates was suspended in a solution of 45 μ L PFDTs in 45 mL *n*-hexane and the mixture was shaken for approximately 30 s. During the reaction time of 30 min, the sedimented suspension was shaken every 5 min to ensure a homogenous coating

of the plates. Subsequently, the modified plates were rinsed at least twice with *n*-hexane.

Preparation of polyhedral liquid marbles:

The polyhedral liquid marbles (LMs) were prepared by simply rolling water droplets over a plate bed on a glass substrate or poly(chlorotrifluoro ethylene) dish. In the case of tetrahedral-, pentahedral- and cube-shaped LMs, they were prepared by rolling 15 μL droplets over individual 2.48 mm plates placed on a hydrophobic surface-roughened poly(chlorotrifluoro ethylene) (CTFE) petri dish. The 15 μL droplets showed an almost spherical shape and could easily roll on the roughened petri dish when tilted by 10–20°. This allowed the droplet to pick up individual plates. Afterwards, the prepared LMs may be transferred to other substrates like glass slides using a (plastic) spoon.

Preparation of jammed polyhedral liquid marbles:

In order to obtain jammed polyhedral LMs with non-equilibrium shapes, LMs prepared in accordance to the previous paragraph (on roughened CTFE petri dish) were either merged, or water was withdrawn from the LM (half of initial volume). Alternatively, a (larger) LM can be prepared and excess amounts of plates are placed on top of the LM. Now the LM can be deformed using a spoon or the like, retaining the deformed shape. To prepare complex structures, the aforementioned techniques are combined to obtain the final result. LMs prepared with the large 2.48 mm and 2.35 mm-sized plates showed such strong interfacial that they could be easily deformed even without the above-mentioned steps (see Movie S1). Photographs were taken using the optical microscope and digital cameras. The colored LMs were dyed using Brilliant Blue (20 mg L^{-1}) and Food Red No. 106 (appears pink, 20 mg L^{-1})

Polymerization of ethyl 2-cyanoacrylate on the air-water interface of polyhedral LMs:

A polyhedral LM (3 μ L, 0.34 mm-sized plates) was placed on a pedestal in a reaction chamber with a vessel containing ethyl 2-cyanoacrylate. The ethyl 2-cyanoacrylate was then heated at 50 $^{\circ}$ C to saturate the gas phase with its vapor. Now, the ethyl 2-cyanoacrylate absorbed and polymerized at the air-water interface, solidifying the interface.^[17] After a reaction time of 30 min the polymerization was finished. Subsequently, the LM was dried up and imaged using the scanning electron microscope (SEM).

Hygroscopic polyhedral liquid marbles:

A polyhedral LM containing $\approx$ 100 μ L of a saturated aqueous LiCl solution was prepared using 0.34 mm-sized plates and placed on a CTFE petri dish. A small watch glass (5 cm diameter) containing 500 μ L water was placed near the LM and the CTFE dish was closed by placing another glass petri dish onto it. For further sealing, Parafilm was applied. Afterwards, the water uptake was observed using an optical microscope for 4 h. Thereafter, the water reservoir was replaced by silica gel and the drying process was observed for 50 h. Finally, the silica gel was replaced by a water reservoir again and the water uptake was observed for 4 h.

Stimuli-responsive polyhedral liquid marbles:

A polyhedral LM (30 μ L aqueous phenolphthalein solution, 1.1 mm-sized transparent plates) was placed on a large glass slide. The phenolphthalein solution was prepared by mixing 10 mL water with 10 μ L 5 wt% ethanolic phenolphthalein solution. A small watch glass (5 cm diameter) containing 200 μ L ammonia solution (28%) was placed next to the LM and both were covered by a glass petri dish. The color change of the LM was observed using the optical microscope. After the color change was completed, the watch glass containing ammonia solution was removed and replaced by a watch glass containing 400 μ L tetrahydrofuran (THF). Absorption of THF and breakage of the LM was observed using the

optical microscope.

Stimuli-responsive polyhedral liquid marbles on water:

A polyhedral LM (15 μL aqueous 3 wt% sodium hydroxide solution, 0.34 mm-sized plates) was transferred to a water surface (50 mL water containing 45 μL 5 wt% ethanolic phenolphthalein solution, in a glass petri dish with a diameter of 10 cm). The LM was moved on the water surface by using an air blower. Afterwards, a total of 330 μL THF was added to the water surface in 5 steps. Digital video cameras (Sony Handycam HDR-CX270 V, 30 $\times$ optical zoom lens and Sony Alpha 7 II, Sony SEL2470Z Zeiss objective) were used to record photographs and movies. The movies were analyzed using commercial software (Keyence VW-9000 MotionAnalyzer) to determine the velocity, acceleration and applied force of the LMs. Using this software, we first determined the position of the center of mass of the LMs in each frame, $r(t)$. We then obtained the finite difference in the position (displacement), $\Delta r(t)$, from the time course of $r(t)$ and the velocity $v(t) = \frac{\Delta r(t)}{\Delta t}$, where Δt is the video rate (1/30 s). From the finite difference in $v(t)$, we obtained $\Delta v(t)$, the acceleration $a(t) = \frac{\Delta v(t)}{\Delta t}$, and the force $F(t) = ma(t)$, where m is the mass of the object. We thereby evaluated the velocity, acceleration and force of the LMs.

Preparation of superhydrophobic surface:

Candle-soot templated superhydrophobic (and superoleophobic) surfaces were prepared according to Ref. 24. The surfaces typically show static contact angles of $>160^\circ$ and $155^\circ \pm 5^\circ$ as well as roll-off angles of $1^\circ \pm 1^\circ$ and $5^\circ \pm 2^\circ$ for 6 μL water and hexadecane, respectively. The receding contact angle of water drops was $>160^\circ$ as well.

Observation of liquid marbles using optical microscope

Polyhedral LMs were observed using an optical microscope with an attached CCD camera (3.0-Megapixels USB Camera GR300BCM2, Shodensha Co., Japan). If not stated otherwise, the LMs were prepared and placed on a hydrophilic glass slide or a CTFE dish and observed under the microscope under various magnifications. The scale bars were obtained by using a micrometer scale ruler. Brightness, contrast and color temperature were adjusted to match between the individual images. For some images, background subtraction using ImageJ was applied.

Observation of liquid marbles using laser scanning confocal microscope

Laser scanning confocal microscopy (LSCM) images were taken using an inverted confocal microscope (Leica TCS SP8 SMD, HC PL APO 40 $\times$ /1.10 CORR CS2 water objective) with a resolution of about 0.3 and 1.0 μm in the horizontal and vertical direction, respectively. A polyhedral LM (15 μL water containing ATTO488 dye, 0.34 mm-sized plates) was placed onto a glass slide (≈ 150 μm thickness) and the lower side of the LM was imaged using the LSCM. The fluorescence of ATTO488 in water is shown in blue and the reflection of light (at the lower side of the plate) is shown in yellow. Reflection and emission signals were recorded simultaneously. It should be noted that the water phase behind the hexagonal plate is not visible because the used plate is non-transparent. Only a strong reflection at the lower side of the plate is visible.

Scanning electron microscopy:

Scanning electron microscopy (SEM) images were taken with a VE-8800 instrument (Keyence, Japan) at gun voltages of 12 kV. To avoid charging, samples were sputter-coated

with gold using an Au coater (SC-701 Quick Coater, Elionix, Japan).

X-ray photoelectron spectroscopy:

X-ray photoelectron spectra (XPS) were acquired using a Kratos Axis Ultra system. The X-ray source was monochromatic Al-K α (source energy: 1486.69 eV). The take-off angle was 0°. The vacuum in the main chamber was below 4·10⁻¹⁰ mbar. The hybrid detector mode was used. Survey spectra were recorded with pass energy of 160 eV. Charge neutralization was applied (current: 2.1 A, balance: 2.8 V, bias: 1.3 V). The survey scans were obtained with 2 scans. The software CasaXPS (Casa Software Ltd.) was used for data elaboration. The binding energies of the XPS spectra were calibrated with the help of the aliphatic C1s peak at 285.0 eV.

Adsorption energy of a plate:

The adsorption energy (ΔG) is defined as the free energy of system required for a plate to desorb from the air-water interface into the air phase ($E_{\text{air}} - E_{\text{interface}}$). It is an important parameter for evaluating the surface activity of plates. E_{air} and $E_{\text{interface}}$ are the energies of systems (air-water interfacial energy + interfacial energy of the plate) where a plate is entirely located in air or at the air-water interface, respectively, and are given by Eqs. (S1) and (S2), respectively.

$$E_{\text{air}} = (3\sqrt{3}s^2 + 6sd)\gamma_{AS} + \frac{3\sqrt{3}}{2}s^2\gamma_{AW} \quad (\text{Eq. S1})$$

$$E_{\text{interface}} = \left(\frac{3\sqrt{3}}{2}s^2 + 6sd\right)\gamma_{AS} + \frac{3\sqrt{3}}{2}s^2\gamma_{WS} \quad (\text{Eq. S2})$$

where s is the side length of the hexagonal plate; d is the thickness of the plate; and γ_{AS} , γ_{WS} , and γ_{AW} are the air-plate, water-plate, and air-water interfacial energies, respectively. Using Eqs. (S1) and (S2), ΔG is given by Eq. (S3).

$$\Delta G = \frac{3\sqrt{3}}{2} s^2 (\gamma_{AS} + \gamma_{AW} - \gamma_{WS}) \quad (\text{Eq. S3})$$

Here, it was assumed that only one large plane of the plate is in contact with water and side planes remained in contact with air. This simple approximation neglects the fact that the drop has a spherical shape while the plate-water interface is planar.

Figure S1. Optical microscopic and scanning electron microscopic (SEM) images of the hexagonal plates. a,b) Optical microscopic images of the plates before (a) and after (b) fluorination treatment with $1H,1H,2H,2H$ -perfluorodecyltrichlorosilane. Scale bar: 500 μm . c,d) Scanning electron microscopic (SEM) images of the fluorinated plates at different magnifications. Scale bars: 40 μm (c), 2 μm (d). e) Side-view SEM images of the fluorinated plates. Scale bar: 40 μm .

Figure S2. X-ray photoelectron spectroscopy (XPS) of the bare and the fluorinated PET substrates.

Figure S3. Zisman plot to evaluate the surface energy of the fluorinated PET plates (here: conducted on fluorinated PET substrate).

Figure S4. Optical microscopic images of large polyhedral LMs. a) Polyhedral LMs prepared with 2.48 mm-sized plates and 120 μL , 480 μL , and 960 μL water droplets. b) Polyhedral LMs prepared with 0.34 mm-sized plates and 120 μL , 480 μL , and 960 μL water droplets (top). Higher magnification images are also shown (bottom).

Figure S5. SEM images of a dried polyhedral PM prepared with 0.34 mm-sized plates and a 3 μ L water droplet after superglue (cyanoacrylate) treatment at different magnifications. The cyanoacrylate polymerizes and solidifies the air-water interface. The position of the polycyanoacrylate layer as well as the air and water phase before drying of the LM are indicated.

Figure S6. Morphology changes of polyhedral LMs during evaporation using different plates.

a) Drying of a polyhedral LM prepared with 0.27 mm-sized plates and 15 μL water. b) Drying of a polyhedral LM prepared with 1.14 mm-sized plates and 15 μL water. Scale bars: 1 mm.

Figure S7. Evaporation of a 15 μL water droplet on a superhydrophobic surface at 22 $^{\circ}\text{C}$ and 45 $\pm$ 5% RH. The droplet continuously decreases its surface area while keeping its spherical shape. Scale bar: 0.5 mm.

Figure S8. a) The evaporation of 15 μL water droplets on a superhydrophobic surface at 21–22 $^{\circ}\text{C}$ and avg. of $37\pm 5\%$ RH follows the expected linear dependence of $V^{2/3}$ vs. time at constant contact angle mode. b) The evaporation of the polyhedral LM at 22 $^{\circ}\text{C}$ and $36\pm 5\%$ RH does not follow the same law.

Figure S9. Optical microscopic images of the transparent PET plates ($A = 2.35 \pm 0.03$ mm, left; $A = 1.13 \pm 0.04$ mm, right) after fluorination with 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane. Scale bar: 500 μ m.

Figure S10. Interfacial jamming of polyhedral LMs. a) A spherocylindrical LM containing $\approx 100 \mu\text{L}$ of a hygroscopic aqueous saturated LiCl solution (0.34 mm-sized plates) exposed to water vapor. The volume of the LM increased over time leading to a decrease of interfacial jamming. The LM resumed to a near-spherical shape. b) The same LM in the presence of silica gel which absorbed water from the atmosphere. The volume of the LM decreased slowly and the LM dried, yet the LM could not return to a cylindrical shape. c) After removal of silica gel and exposure to water vapor, the LM resumed to the near-spherical shape again due to water uptake. Scale bars: 2 mm.

Figure S11. NH_3 -induced color change of polyhedral LMs. a) The ammonia gas penetrated through the gaps between the plates of a 30 μL polyhedral LM prepared using 1.13 mm-sized transparent plates. Therefore, there was a slight color gradient between the edges and the middle in the aqueous solution underneath the plates. The edges show a stronger coloration compared to the middle. b) Optical microscopic image of a 400 μL polyhedral LM prepared with 2.35 mm-sized transparent plates in a highly jammed state clearly shows that the vapors penetrated between the gaps of the plates.

Figure S12. THF-induced breakage of a polyhedral LM. a) Stimuli-responsive 30 μL polyhedral LM (0.34 mm-sized plates) containing dyed water broke after 5–6 min exposure to THF vapor. b) Backside view of broken liquid marble. The liquid marble broke on the bottom left edge (marked with white dots) and the liquid spread over the glass slide afterwards. It is apparent that the liquid marble was covered by only one monolayer of plates. Scale bars: 2 mm.

Figure S13. Broken polyhedral LM containing $\approx 60 \mu\text{L}$ aqueous saturated LiCl solution floating on a water surface. The magnifying effect of the water droplet on top of the plates allows close observation of the plates separating the two air-water interfaces.

Descriptions for the Movies:

Movie S1. Formation of a jammed polyhedral LM on 2.35 mm-sized transparent plates using dyed water and shaping of the LM into liquid letters “N” and “L” using a syringe needle within a few seconds.

Movie S2. Polyhedral LM (15 μ L 3 wt% NaOH solution, 0.34 mm-sized plates) on a water surface driven by air blows and disruption of the LM by consecutive addition of THF. The pH change induced by disruption of the LM leads to the color change of the water reservoir (containing phenolphthalein) from colorless to pink.

References:

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Supporting Information
Movie S1 - Letters.mp4

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Supporting Information

Movie S2 - PHLM on water.mp4