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# Hydrophobic Hydrogels with Fruit-like Structure and Functions

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## Abstract

Normally, a polymer network swells in a good solvent to form a gel but the gel shrinks in a poor solvent. Here, for the first time, we report an abnormal phenomenon: some hydrophobic gels significantly swell in water, reaching water content as high as 99.6 wt% at most. Such abnormal swelling behaviors in the non-solvent water are observed universally for various hydrophobic organo-gels containing omniphilic organic solvents that have a higher affinity to water than to the hydrophobic polymers. The formation of semi-permeable skin layer due to the rapid phase separation, and the asymmetric diffusion of water molecules into the gel driven by the high osmotic pressure of the organic solvent-water mixing, are found to be the reasons for such abnormal swelling. As a result, the hydrophobic hydrogels have a fruit-like structure, consisting of hydrophobic skin and water-trapped micro-pores, to display various unique properties, such as significantly enhanced strength, surface hydrophobicity, anti-drying, despite their extremely high water-content. Furthermore, the hydrophobic hydrogels exhibit selective water absorption from concentrated saline solutions and rapid water release at a small pressure as like to squeeze juices from fruits. These novel functions of hydrophobic hydrogels will find promising applications, for example, as materials that can automatically take the fresh water from seawater.

Keywords: Hydrophobic hydrogel, Phase separation, Semi-permeable skin, Asymmetric diffusion, Seawater desalination

Polymer gels are defined as cross-linked polymer networks that are swollen in solvents. Since the last 3 decades, gels, especially water-based hydrogels, have embraced increasing interest for the numerous engineering and biological applications, including bio-engineering,<sup>[1-2]</sup> adhesion,<sup>[3-4]</sup> soft robotics,<sup>[5]</sup> and 3-D printing.<sup>[6]</sup> Ordinarily, a polymer network swells in a good solvent having a high affinity to polymer, forming a gel. When experiencing solvent exchange from good to poor, a gel usually exhibits a monotonous deswelling with time if the good and poor solvents are miscible.<sup>[10-11]</sup> During this process, the good solvent easily escapes from gels driven by osmotic pressure of solvent-solvent mixing, while the poor solvent hardly enters the gel due to the demixing of polymer and poor solvent (**Figure 1a**). Here, we report an abnormal swelling of hydrophobic gels in water to form “hydrophobic hydrogels”. We discovered that when hydrophobic gels swollen with omniphilic organic solvents are immersed in water or aqueous solutions, instead of shrinkage, the hydrophobic gels substantially swell to reach a water content as high as 99.6 wt% at most. The significant swelling of hydrophobic gels in water leads to the formation of a novel class of “hydrophobic hydrogels” that have a unique fruit-like structure and show unique functions such as selective water absorption. To our knowledge, such abnormal swelling phenomenon of hydrophobic gels in water has never been reported before. This abnormal swelling is attributed to the rapid formation of a semi-permeable skin layer on the surface of the gel by the phase separation of the hydrophobic polymer in water, which brings about a strongly asymmetrical diffusion for the organic solvent and water. The impermeable organic solvent is effectively trapped inside the gel, and thus generates a high osmotic pressure which drives the permeable water to diffuse into the gel robustly. The water absorption of the

hydrophobic gels causes phase separation to form porous structure inside the gels (**Figure 1b**).

*Abnormal swelling phenomenon in water.*

As an example, we first show the different swelling behaviors of hydrophobic poly(methyl acrylate) (PMA) gels containing two different omniphilic organic solvents, tetrahydrofuran (THF) and dimethylsulfoxide (DMSO) (**Figure 1c, d**). The covalently crosslinked PMA gels were initially prepared in DMSO and subsequently swollen in THF or DMSO until equilibrium. Although the dry PMA network barely swells in water,<sup>[13]</sup> its organic gels exhibit very different behaviors. After being immersed in water, both gels experienced a fast phase separation by water infusion: the originally transparent gels rapidly turned to opaque and then white, starting from surfaces. However, they exhibited striking differences in volume change. The PMA-THF gel monotonically shrank with time, as commonly expected for a swollen gel immersed in a poor solvent that is miscible with the original solvent in the gel (**Figure 1c, e** and **video S1**). After 30 min, the PMA-THF gel shrank to only 20% of its initial size in water. In contrast, the PMA-DMSO gel surprisingly increased its volume rapidly with time in water, indicating that a large amount of water was absorbed by the hydrophobic PMA gel (**Figure 1d, e** and **video S2**). After 8 hours, the volume of the gel boosted more than 5 times of its initial value in DMSO, and the water content reached a level as high as 99 wt%. The abnormal swelling in water is reversible, and it can be repeated by cyclically exchanging the solvent from DMSO to water for many times (**Figure S1**, Supporting Information). The organo-gels always exhibit swelling performance after immersion in water. However, the swelling ratio of the gels in water gradually decreases with the increase of the cycle number, especially at the second cycle, probably due to some damage of the pristine sample upon the

significant swelling in the first cycle. Interestingly, while the DMSO-swollen PMA gel is soft and showing a mechanical response typical of rubbery materials (**Figure 1f**), the gel becomes much stiffer and stronger after significant swelling in water. The strengthening of the hydrophobic hydrogel can be attributed to the strain-hardening of the polymer chains induced by remarkable volume expansion as well as the meso-scale aggregated structure formed by phase separation.<sup>[10, 12]</sup>

It is well established that, the swelling of a polymer network in a good solvent is driven by the gain in the free energy of mixing between the polymer and the solvent, and a swelling equilibrium is reached when this mixing energy gain is counter-balanced by the elastic energy of the polymer chains. In a poor solvent, the polymer and the solvent phase separate and the equilibrium swelling dramatically decreases. Therefore, the observed swelling of PMA-DMSO gel in water that is a poor solvent of the PMA cannot be explained by this thermodynamic equilibrium theory. To reveal the driving force for the absorption of water into the hydrophobic PMA network, we analyzed the amount of organic solvent in the gels as a function of swelling time. As shown in **Figure 1g**, the amount of THF in the gels decreased rapidly: only about 1% of THF relative to the initial amount remained in the gel after 4 h of immersion in water. However, the amount of DMSO maintained an elevated level and about 20% of DMSO still remained in the gel even after 4 days despite the frequent refreshing of the water bath. Since both organic solvents are completely water miscible, the significant difference in the amount of residual organic solvents brings about significant differences in osmotic pressure. That is, for the THF-swollen PMA gel, the negligible amount of THF in the PMA gel contributes insignificantly to balance the desolvation of the hydrophobic PMA in water, thus the gel shrank. In contrast, the large amount of remaining DMSO generates a large osmotic pressure to

imbibe the water and swell the gel, as like the effect of counter-ions on the swelling of polyelectrolyte gels. This osmosis-driven swelling is further confirmed by immersing the PMA-DMSO gel in various aqueous solutions containing DMSO to increase the osmotic pressure of the bath solution. The gels exhibited a lower swelling capability at a higher DMSO concentration aqueous solution (**Figure S2**), which confirms the osmosis effect.

The extremely low release rate of DMSO implies that a semi-permeable structure, easily permeable to water but hardly to DMSO, is formed on the surface of the gel with the polymer phase separation, which leads to the asymmetric diffusion. In fact, without polymer phase separation, a hydrophilic poly(hydroxyethylacrylate) (PHEA) gel swollen in DMSO lost the organic solvent readily in water (**Figure S3**).

The PMA-DMSO gel also swells in saline solution, and the semi-permeable skin layer is hardly permeable to ions. In 10 wt% alkali chloride salt solutions, the gel still attains a swelling around 4 times by volume regardless the high osmotic pressure of the saline solution (**Figure 1h**, insert). The concentration of ions inside the swollen hydrophobic hydrogel is only 0.1 ~ 1% of that in the bath solutions, displaying a slightly higher selectivity to  $\text{Na}^+$  and  $\text{Li}^+$  ions having larger hydrodynamic radius  $R_h$  than to  $\text{K}^+$  ion (**Figure 1h**). These results support the hypothesis of a semi-permeable structure formation: the hydrated ions, which have much larger radii than water, can hardly pass through the semi-permeable structure. Accordingly, the phase separation induces a condensed polymer structure to show the semi-permeable effect. When certain amount of defects was introduced into the membranes by copolymerization of hydrophilic segments with the hydrophobic MA, the swelling of the gel in water was suppressed, although the relative hydrophilicity of the gel was increased (**Figure S4**).

***Condition for the abnormal swelling.***

Why was the semi-permeable skin layer formed in the DMSO gel but not in the THF gel that also exhibited a phase separation? Or more generally, what is the general requirement on the organic solvents to show the abnormal swelling phenomenon? To answer these questions, we further investigated the behavior of the PMA gels in six other omniphilic organic solvents, and the results are shown in **Figure 2a**. The PMA gels pre-swelled in DMF (*N,N*-dimethylformamide), NMP (*N*-methyl-2-pyrrolidone), DMAc (*N,N*-dimethylacetamide), or NMF (*N*-methylformamide) showed a significant swelling in water, in similar to the behavior observed for DMSO. In contrast, the PMA gels pre-swelled in acetone and MeCN (acetonitrile) shrank in water, as was the case for THF. Among the different samples tested, the maximum swelling ratio, which was attained by the PMA-DMAc gel, reached about 2 orders of magnitude higher than PMA-THF or PMA-MeCN. In agreement with the results shown in **Fig. 1g**, the swelling capacity clearly correlated to the residual level of organic solvents (**Figure S5a**). From the swelling behavior and the residual solvent level in the hydrogels, these organic solvents can be classified into two categories: “swelling solvents”, such as DMSO, DMF, NMP, DMAc, and NMF; and “shrinking solvents”, such as THF, acetone, and MeCN. While all these organic solvents have comparable physical properties (e.g. molecular size, dielectric constant, solubility parameter), their relative affinities with water and polymer are remarkably different, as measured by the partition-coefficient test (**Figure 2a**). All the “swelling solvents” have much stronger affinities with water than with the monomer MA ( $P_{\text{water/MA}} \gg 1$ ), while all “shrinking solvents” display comparable affinities between water and MA ( $P_{\text{water/MA}} \sim 1$ ). These results agree with the mixing enthalpy of the organic solvent and water. That is, the “swelling solvents” have much higher affinity to water than “shrinking solvents”.<sup>[14-19]</sup> Meanwhile, all the solvents investigated show no significant

difference in their affinity to the PMA network, as seen from the comparable equilibrium swelling ratio of PMA gels in these solvents (**Figure S5b**).

***Universality of the abnormal swelling.***

To clarify the universality of this abnormal swelling phenomenon, we further studied the swelling behavior of eleven organo-gels from different hydrophobic polymers. These gels were initially swollen in “swelling solvent” DMSO or DMF. As shown by the partition coefficient  $P_{\text{water/monomer}}$  in **Figure 2b**, the affinity of the organic solvents to water is always higher than to the corresponding monomers of these eleven gels. All of these organo-gels displayed swelling in water, as like the PMA organo-gel, and the highest water content reached 99.6% for poly(benzyl acrylate) (PBnA). The above results show that the abnormal swelling is a general phenomenon for a hydrophobic network pre-swollen in an organic solvent that has a higher affinity to water than to the polymer segment.

While all these hydrophobic organo-gels exhibited swelling in water, the long-time swelling profiles varied with the relative relationship between the swelling temperature ( $T_{\text{obs}}$ ) and the glass transition temperature ( $T_g$ ) of the polymer (**Figure S6a**). The gels from PMA polymers with  $T_g < T_{\text{obs}}$  (room temperature) swelled in water and reached their maximum volume after several days, and then gradually decreased in volume at a quite low rate, exhibiting no swelling equilibrium. By contrast, the gels from poly(phenyl acrylate) (PPA) polymers with  $T_g > T_{\text{obs}}$  exhibited an equilibrium swelling but with a relatively low swelling ratio at equilibrium. We consider that the deswelling at the long-time scale for polymers with  $T_g < T_{\text{obs}}$  is due to the continuous leakage of the organic solvent, which reduces the osmotic pressure. As the swelling is controlled by the competition between the osmotic pressure of the trapped organic solvent and the contractile elasticity of the gel, the leakage of the

organic solvent reduces the osmotic pressure and results in the deswelling at long time scale. On the other hand, the less swelling ability and swelling saturation for polymers with  $T_g > T_{obs}$  can be attributed to the plasticity of the phase separation structure during swelling, which increases the swelling resistance but diminishes the contractile elasticity. As a result, the gel maintained a constant volume even all of the organic solvents diffused out of the gel (**Figure S6b**). After a prolonged time in water, we can obtain highly swollen hydrophobic hydrogels with negligible amount of residual organic solvent.

### ***Structure observation.***

To reveal the structure evolution during the abnormal swelling of the hydrophobic gel in water, we observe the cross-section of the disc-shape samples through the thickness direction (**Figure 3a, upper**). **Figures 3b** and **3c** show the observation on a PMA-DMSO gel (initial diameter  $d=35$  mm and thickness  $t=2$  mm) swollen in water for 8 h. Under polarized optical microscope, a strong birefringence is observed in the outer layer near surface of several hundreds of microns, indicating that orientated structure is formed near the surface (**Figure 3b**). Laser microscope observation further reveals that the oriented structure is attributed to an elongated morphology aligned vertical to the surface plane (**Figure 3c**). Beneath this vertically aligned layer, an isotropic layer containing large bubbles is observed. Close to the center of the sample, a relatively smooth morphology with small bubbles aligned slightly parallel to the surface is observed. The elongated outer layer starts to form around 0.5 h, becomes thicker with time, and then blurs to show an obscure boundary between different layers (**Figure S8a**). At 4 days when the swelling ratio reaches the maximum (**Figure S7a**), the center layer completely disappears to show isotropic morphology. After that, the gel keeps the isotropic morphology during the slow deswelling process.

The layered morphology formed during the swelling process reveals the kinetics of water diffusion during the solvent exchange process. At the early stage, the outer layer near surface swells while the inner layer is unswollen, which generates an internal stress mismatching. As a result, the swollen outer layers receive a compression from the unswollen inner layer, leading to the elongated shape of outer layer aligned vertically to the surface, as shown by **Figure 3b, c**. In turn, the inner layer receives a tension from the swollen outer layer to show slight orientation parallel to the surface.

In order to clarify the microstructure, we performed scanning electron microscope (SEM) observation of a PPA (poly(phenyl acrylate)) hydrogel after freeze-drying. The high  $T_g$  of PPA (63 °C) can maintain the structure after dehydration of the hydrophobic hydrogel, which makes it suitable for structure observation. SEM images reveal that the outermost surface of the sample is covered by a thin dense layer of a few microns thick (**Figure 3d**). Beneath this dense skin layer, a porous layer with slight anisotropy aligned vertical to the surface, of hundred microns thick, is observed. The dense surface layer is the strong evidence of the semi-permeable skin layer, while the anisotropic porous layer well corresponds to the swelling outer layer revealed by the optical observation (**Figure 3a, lower**).

For a ternary system composed of polymer, good solvent, and poor solvent in which the two solvents are miscible, it has been reported that instantaneous demixing occurs when the good solvent has a high affinity to the poor solvent, and a structure composed of a dense skin layer of several  $\mu\text{m}$  thick and oriented porous layer of hundred  $\mu\text{m}$  thick aligned vertical to the surface is formed for a polymer membrane.<sup>[20-23]</sup> On the other hand, delayed demixing occurs when the good solvent has a low affinity to the poor solvent, and open porous structure is formed. Here, similar thing happens. When immersing the hydrophobic organo-gel in water, the

“swelling solvents” induce instantaneous demixing to form a condensed semi-permeable membrane on the gel surface. At molecular level, these “swelling solvents” have larger size than water. Moreover, the strong interaction between the “swelling solvents” and water results in plausible clusters. Once the clusters are formed, the “swelling solvents” are further immobilized and the size discrimination between DMSO/water cluster and water molecular is more remarkable, therefore these organic solvents diffuse much slower than water across the membrane. In contrast, the “shrinking solvents” results in delayed demixing to form open porous structure, which releases the organic solvent quickly.

Due to the formation of the layered structure, swelling kinetics of the hydrophobic gels in water is anisotropic. For a disc-shape sample of diameter  $d=35$  mm and thickness  $t=2$  mm, the degree of anisotropy  $A$ , defined as the ratio of relative size change in diameter to thickness,  $A= (d'/d)/(t'/t)$ , firstly increases to 1.3 and then gradually decreases to a value near 1 (**Figure 3e**). This indicates that the diameter increases faster than the thickness ( $d'/d > t'/t$ ) at the initial swelling stage, which is opposite to that for normal swelling of a gel in good solvents. This is because the outer swollen layer with elongated pore structure is stiffer than the inner unswollen layer, as revealed in **Figure 1f**, therefore the inner layer is more prone to deform to show anisotropic swelling. Using a simple “sandwich structure” model (Supporting information), in which the two outer layers are more rigid and swollen than the middle inner layer, and the outer layers become thick with time, the time profile of the experimental swelling anisotropy are reproduced satisfactorily (**Figure 3e**, dash line). In addition, the “sandwich” model also reproduces the time evolution of the fraction of swollen outer layers in relative to the whole sample thickness (**Figure S7b**).

To study the effect of the semi-permeable skin layer on the abnormal swelling, we further carried out the swelling experiment in water with disc-shape PMA organo-gels of constant diameter ( $d=35$  mm) but different thicknesses ( $t = 0.7\sim 6.5$  mm). The time profiles of the swelling ratio are depicted in **Figure 3f**, in which the swelling time is normalized by the square of the initial sample thickness ( $\text{time}/t^2$ ). During the swelling process, thinner sample shows a smaller swelling than the thick sample for the same normalized time, while the maximum swelling ratio and the deswelling kinetics collapsed to a master curve. These results indicate that the maximum swelling ratio is independent of thickness, while the time to reach the maximum swelling increases with the square of thickness. The systematic deviation of swelling ratio to smaller value for thinner sample in the master curve indicates that the effect of the surface skin layer. Since the thickness of the skin layer is independent of the total sample thickness, the thickness fraction of skin layer increases with the decrease of the sample thickness, leading to more retardation effect to swelling ratio. On the contrary, the collapse of the kinetic profiles in the deswelling process features a simple diffusion in a homogeneous gel, which well agrees with the structure observation (**Figure S7a**).

The above results indicate that when an organo-gel is immersed in water, a dense skin layer of several microns-thick is formed on the surface due to instantaneous demixing of polymer and water. This skin layer serves as a semi-permeable membrane to suppress the diffusion of the organic solvent to the bath while the diffusion of water molecules is less affected. As a result, the water molecules diffuse into the gel, driven by the high osmotic pressure generated by the trapped organic solvent. With the increase of water content inside the gel, local phase separation occurs to form porous

structure inside the gel. Due to the large swelling and stiffening of the two outer layers, the gel swells faster in lateral direction, exhibiting an anisotropic swelling.

### ***Unique functions and possible applications***

The hydrophobic hydrogels exhibit various unique functions which may greatly broaden their applications. For example, regardless of the extremely high water content, the PMA hydrogels have a hydrophobic surface, showing a static contact angle of  $92\pm 3^\circ$  to water (**Figure S8**), which is much higher than that of common hydrogels with an equivalent water content.<sup>[24]</sup> Thus, the hydrophobic hydrogels have a structure consisting of a hydrophobic dense skin and micropores containing trapped waters, a structure similar to fruits such as an orange. Such structure significantly delays the evaporation of water molecules from the hydrophobic hydrogels in comparison with conventional hydrogels from hydrophilic polymers (**Figure 4a**). As presented in **Figure 4b**, a conventional hydrogel from poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) quickly dried in the fume hood within 1 day, whereas the PMA hydrophobic hydrogel stored in the same condition still maintained 10% of water after one week. Moreover, as like a fruit, the water in the hydrophobic gels can be quickly squeezed out with a small pressure (**Figure 4c**). This is very different from the conventional hydrophilic hydrogels where high pressure and long-time are required to squeeze the water from the hydrogel since water is hydrated with the nano-scale polymer network.<sup>[25]</sup> Combining the previously described property of selective water absorption in saline solutions, the hydrophobic hydrogels are promising materials for energy-free sea water desalination or marine lifesaving. As demonstrated in **Figure 4d-e** and **Video S3**, an PMA-DMSO organo-gel spontaneously absorbs large amount of water from a 3 wt% NaCl saline solution, while left nearly all the solutes in the swelling media. Then, with a household

squeezer, salt-free water can be easily squeezed out from the gel without breaking of the gel.

As the abnormal swelling of hydrophobic gels in water is universal, numerous hydrophobic polymers can be applied to develop water containing materials. The various unique properties of the hydrophobic hydrogels make them as novel promising materials for applications in biomedical, agricultural, and industrial fields.

### **Experimental Section**

Experimental details are provided in the Supporting Information.

### **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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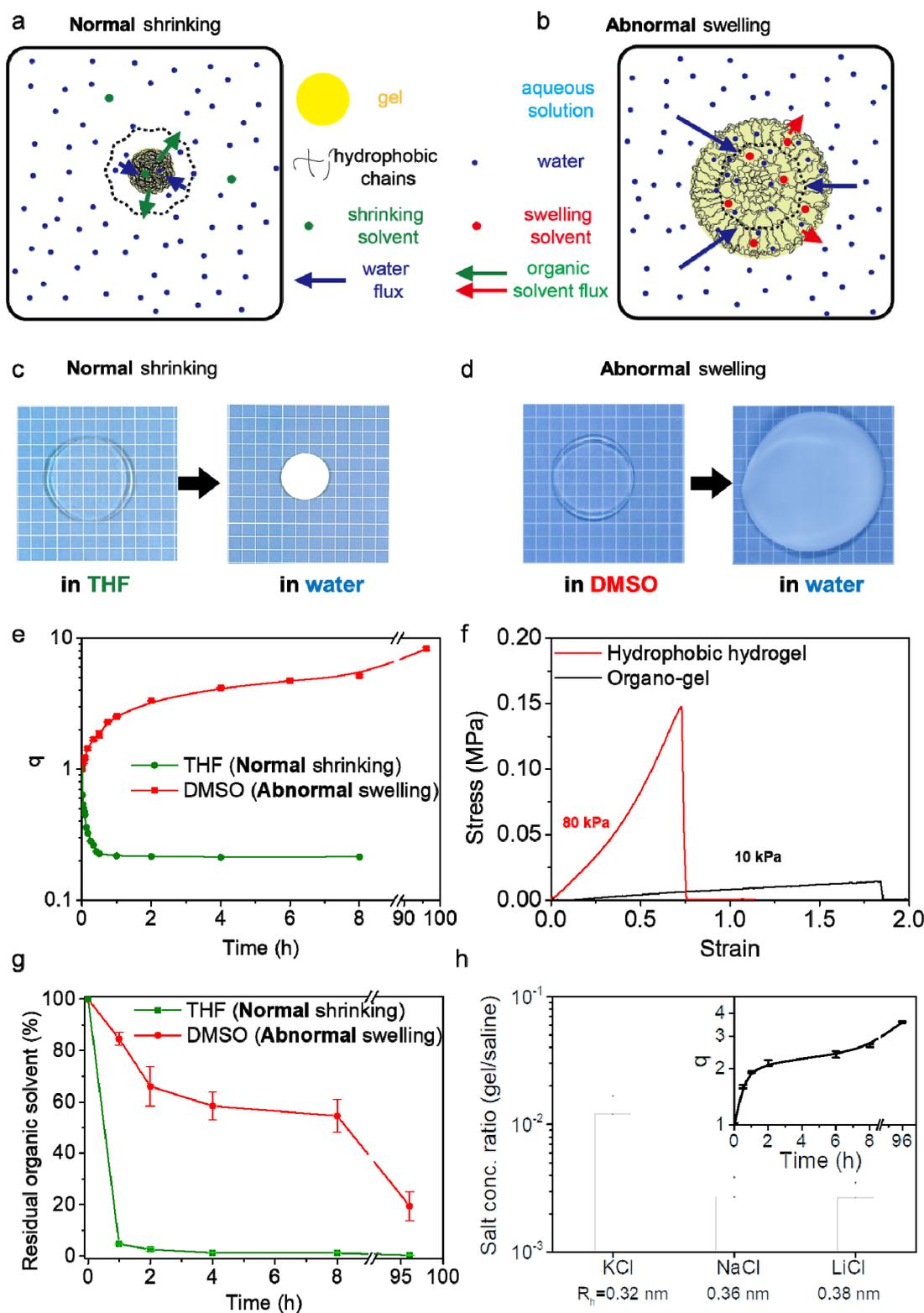
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**Figure 1** (a-b) Schematic illustration of organo-gels' volume change upon solvent exchange and the formation of "hydrophobic hydrogels". When organo-gels constructed from hydrophobic network pre-swelled in an omniphilic organic solvent are immersed in water, phase separation occurs. Depending on the relative affinity of the organic solvent to the polymer and water, normal shrinking (a) or abnormal swelling (b) of the organo-gel in water occurs (The dash line in figures illustrated the initial size of organo-gels). In the normal case, the diffusion of the organic solvent and

water leads to gel shrinking due to phase separation. In the abnormal case, robust phase separation results in the formation of semi-permeable structure to trap the organic solvent inside the gel. As a result, the gel substantially swells by the high osmotic pressure of the organic solvent. (c) Photograph of normal shrinking: PMA organo-gel at equilibrium state in THF (left) and after immersing PMA-THF organo-gel in water for 8 h at 25 °C. (d) Photograph of abnormal swelling: PMA organo-gel at equilibrium state in DMSO (left) and after immersing PMA-DMSO organo-gel in water (right) for 8 h at 25 °C. (e) Time profiles of swelling ratio ( $q$ ) of PMA organo-gels from THF and DMSO after being immersed in water at 25 °C. The initial size of the disc shape samples was 35 mm in diameter and 2 mm in thickness. (f) Uniaxial tensile behaviors of the PMA-DMSO organo-gel (figure d, left) and its PMA hydrogel (figure d, right). The Young's moduli of the two gels are shown beside the curves. (g) Time profiles of the residual organic solvent in the PMA organo-gels after being immersed in water. The residual organic solvent ratio is defined as the amount of organic solvent relative to the initial state. (h) Salt concentrations inside PMA hydrogels over that in saline solution after being swelled in saline solutions (10 wt%) for 4 days at 25 °C. The hydrated radii ( $R_h$ ) of cations are illustrated below the columns, noting that the cations have bigger radii than the anion. The inserting figure shows the time profile of swelling ratio ( $q$ ) of the gel in 10 wt% (1.7 M) NaCl solution.

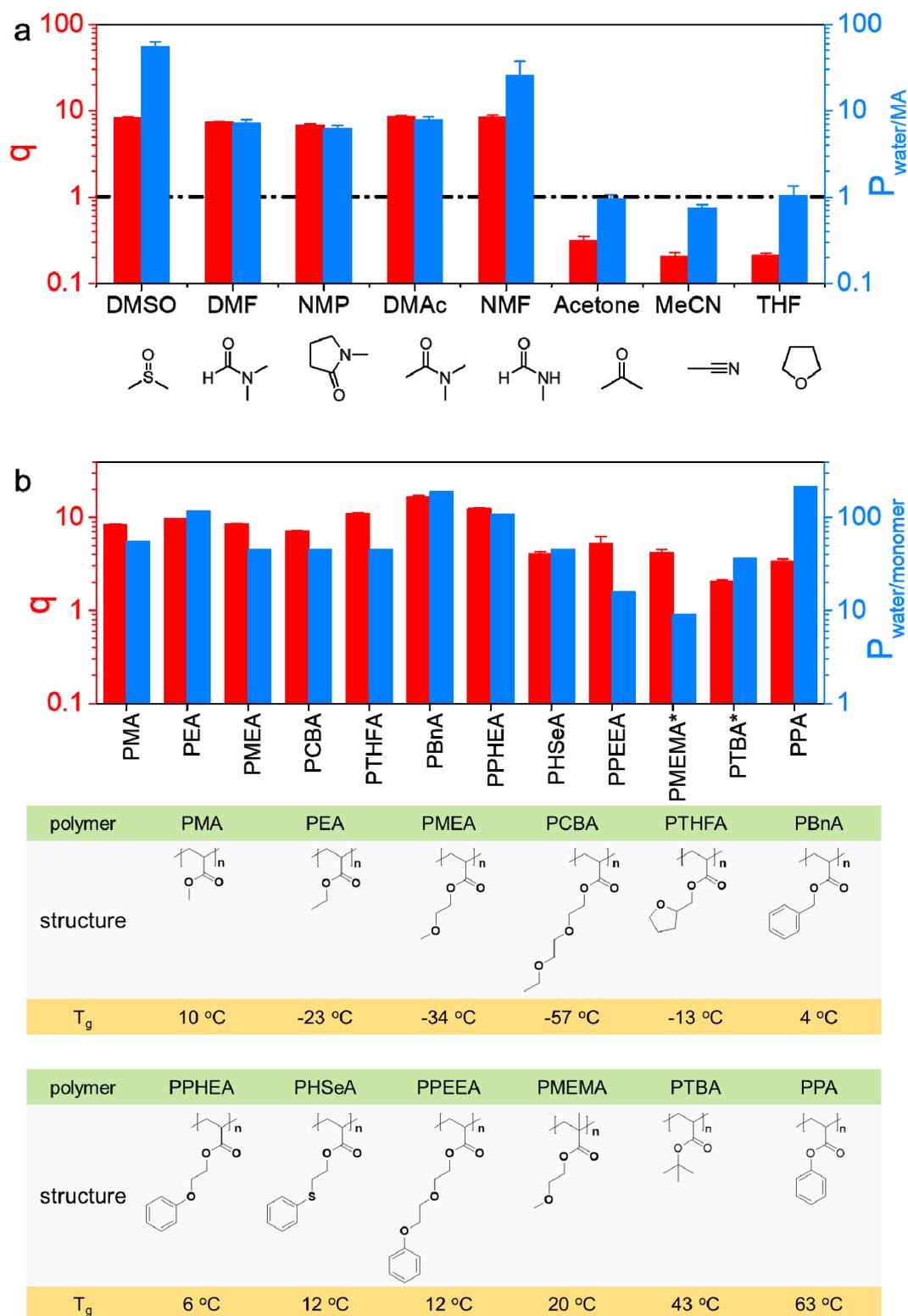


Figure 2 Generalization of the abnormal swelling of organo-gels in water. (a) Solvent effect. Red column: maximum swelling ratio ( $q$ ) of PMA gels starting from organo-gels in different solvents at 25 °C; blue column: partition coefficient ( $P_{\text{water/MA}}$ ) of different organic solvents in water over that in MA.  $q = 1$  means that the gels volume remains unchanged, and  $P_{\text{water/MA}} = 1$  means that the organic solvents have the same affinity for water and MA (guided as dash line). Chemical structures of solvents are illustrated below the figure. All the organo-gels were initially synthesized in

DMSO and immersed in different solvents until equilibrium state. (b) Polymer effect. Red column: maximum swelling ratio of different organo-gels in water at 25 °C. The organo-gels were pre-swelled in DMSO (except for PMEMA and PTBA, which were pre-swelled in DMF). Blue column: partition coefficient ( $P_{\text{water/monomer}}$ ) of DMSO in water over that in different monomers (in the cases of PMEMA and PTBA, DMF was used in the place of DMSO). Chemical structures of polymers and glass transition temperature ( $T_g$ ) of the linear polymers are illustrated below the figure.

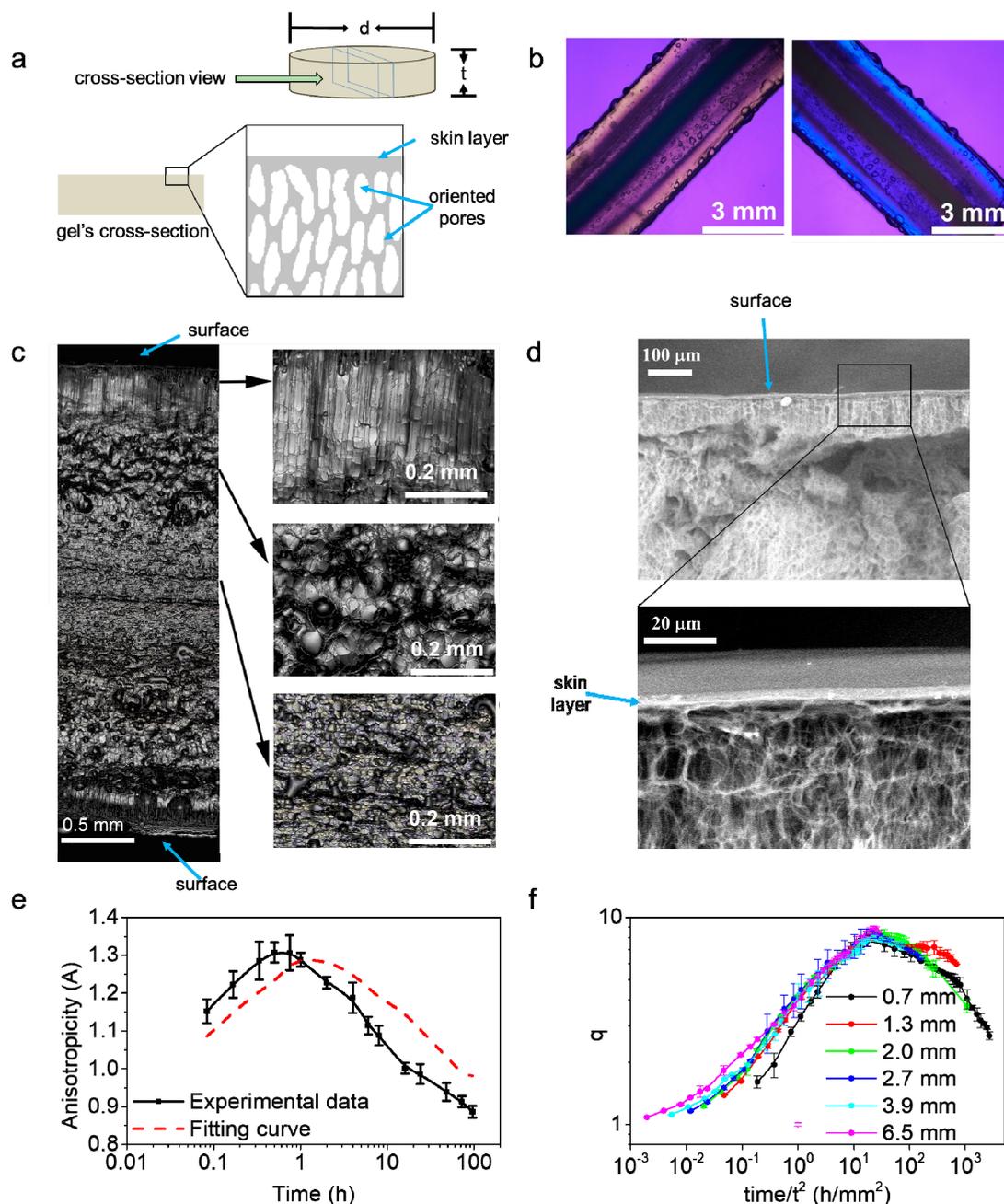


Figure 3 Structure analysis and anisotropic swelling kinetics of PMA-DMSO gels in water. (a) Dimension of disc-shape gel used for swelling and structure observation (upper) and illustration of the skin layer and oriented porous structure revealed by the structure analysis (lower). (b) Polarized optical microscope images of sample' fresh cut cross-section perpendicular to the disc surface at  $+45^\circ$  and  $-45^\circ$  rotation with the 532 nm sensitive tint plate. (c) 3-D laser microscope images of the fresh cut cross-section of hydrophobic hydrogel during swelling. The samples in (b-c) were obtained by immersing the organo-gel ( $d=35$  mm diameter,  $t=2.0$  mm thickness) in water for 8 h at  $25^\circ\text{C}$  and then cutting a slab ( $\sim 1$  mm thickness). (d) SEM cross-section view of a PPA-DMSO gel swelled in water for 40 days. The zoomed-in image clearly shows that a dense skin layer of  $\sim\mu\text{m}$ -thick is formed on the top of the porous surface layer of  $\sim 100\ \mu\text{m}$ . (e) Swelling anisotropy of discoid organo-gel in water. The swelling anisotropy ( $A$ ) is the swelling ratio of the diameter divided by that of the thickness ( $A=(d'/d)/(t'/t)$ ). The red-dashed curve was obtained from a

“sandwich structure” model using proper fitting parameters (see Supporting Information). (f) Size dependence of swelling kinetics at 25 °C: master curve of swelling kinetics of discoid organo-gels with different initial thickness  $t$  while the initial diameters  $d$  of the gels was fixed at 35 mm.

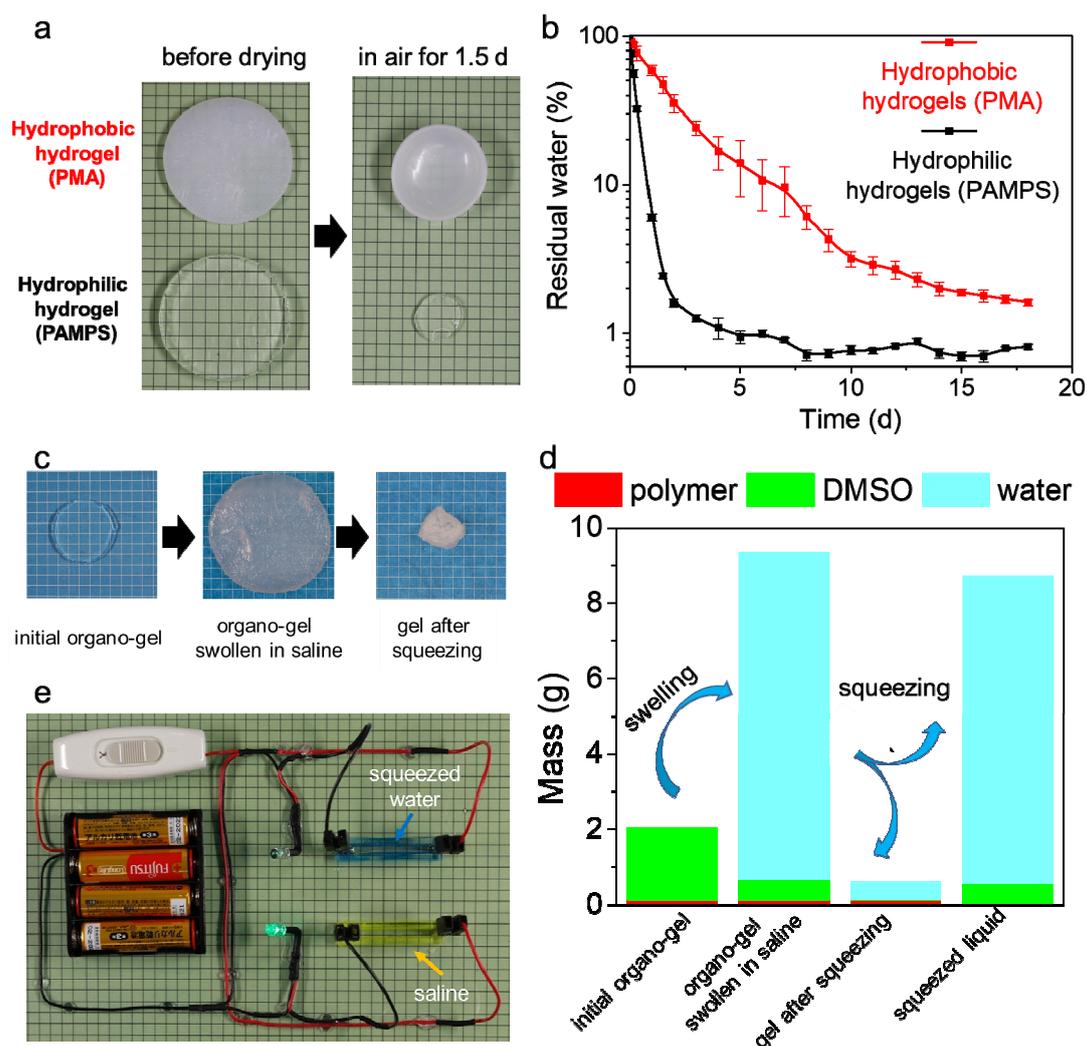


Figure 4 Demonstration of water retention, desalination and recovery. (a) Images to show the difference of water retention capacity between a hydrophobic PMA hydrogel and a hydrophilic PAMPS (Poly(2-acrylamido-2-methyl-1-propanesulfonic acid)) hydrogel at 25 °C. Both hydrogels have the same initial size ( $d=50$  mm,  $t=4$  mm) and comparable water content (99 wt%). (b) Retained water ratio of a hydrophobic PMA hydrogel and a hydrophilic PAMPS hydrogel at 25 °C in fume hood (humidity: 40%). (c) Photos of the organo-gel at initial state, organo-gel swollen in saline solution (NaCl, 3 wt%) for 48 h, and the gel after being compressed with normal compressive stress  $\sim 0.5$  MPa for 2 s. (d) Compositions of the initial organo-gel, the gel after swollen in saline, the gel after squeezing, and the squeezed liquid. Note that the salt in the swollen gels and squeezed liquid could not be detected within the experimental accuracy, indicating a high selectivity to water absorption. (e) Photograph demonstrating the low salt content in the squeezed liquid from the hydrophobic hydrogel. The swelling media (NaCl saline, 3 wt%, yellow channel) has a high electric conductivity to light the bulb while the squeezed liquid from the hydrophobic hydrogel (blue channel) could not due to low conductivity.

## Table of content

We discovered that hydrophobic networks containing omniphilic organic solvents abnormally swell in water to form hydrophobic hydrogels with high water-content (99.6 wt% at most). The hydrophobic hydrogels, having a fruit-like structure with a semi-permeable skin layer and water-trapped micro-pores, display unique properties, including enhanced strength, surface hydrophobicity, anti-drying, despite their extremely high water-content. The abnormal swelling is applied to extract water from saline solution.

Keywords: Hydrophobic hydrogel, Phase separation, Semi-permeable skin, Asymmetric diffusion, Seawater desalination

