Supporting information

Movie S1. Droplet dissolution from -6 to 4 s, where time zero is defined in Fig. 4d. Played at real time.

Movie S2. Droplet condensation from 0 to 150 s, where time zero is defined in Fig. 4g. Played at 8X.

Movie S3. Uniformly distributed coacervate droplets in a hydrogel.

Movie S4. Locally distributed coacervate droplets in a hydrogel.
Figure S1. Molecular structures of DTAB, PTS, and β-CD.
Figure S2. Pictures of DTAB/PTS coacervate suspensions in cuvettes under white (left) and UV light (right). The suspension is turbid and fluorescently cyan in its newly formed state (a). A transparent, fluorescently cyan bottom phase coexists with a clear, fluorescently blue upper phase after complete sedimentation (b). A highly concentrated sample is used in b to stress the bottom phase while a typical upper-to-lower phase volume ratio is ~1000:3 in the case of 10 mM DTAB and 2.5 mM PTS. The bottom phase fully is dissolved after β-CD addition (c).
Figure S3. Fluorescence of PTS. a, Fluorescence spectra of 0.01 mM PTS in the presence of different concentrations of DTAB. The solution is always clear and no macroscopic coacervation is observable. b, Fluorescence spectra of the upper (blue curve) and lower (cyan curve) phases after complete phase separation.
Figure S4. Properties of the DTAB/PTS coacervate droplets. a, Phase diagram of the DTAB/PTS/β-CD system. Regions inside the curves are coacervation regions as determined by sample turbidity. Black dashed line indicates charge neutral mixing. The coacervate region (red line) is centered around the charge-neutral line and expanding with higher concentrations of DTAB and PTS. Addition of β-CD shifts the coacervation region to the right with roughly constant shape and size. b, Zeta potential of the droplets as a function of PTS concentration with black, red, and blue points corresponding to 5, 10, and 15 mM of DTAB, respectively. Surface charge of the droplets can be systematically tuned by changing the DTAB/PTS ratio. c, Dependences of optical density on NaCl concentration (black points, DTAB/PTS 5/1.25 mM) and on temperature (blue points, DTAB/PTS 2.5/1.25 mM). Addition of NaCl screens electrostatic interactions and gradually dissolves the coacervates, while heating favors coacervation. Such dependences signify electrostatic attraction and entropy as drive forces for coacervation, in agreement with previous literatures. d, Table of partition ratio of solute in the coacervate phase (see Methods for
details). The positive coacervate is DTAB/PTS 10/1 mM with 33 mV zeta potential, while the negative
one is DTAB/PTS 10/3.5 mM with -30 mV zeta potential. AH and LR B stand for acriflavine
hydrochloride and lissamine rhodamine B, respectively. The hydrophobic dye, nile red, is of infinite
partition ratio as its solubility in water phase is negligible. The current coacervates exhibit remarkable
capacity to concentrate and compartmentalize a variety of small molecules, proteins, and nanoparticles
Partitioning ratios of charged and hydrophobic dyes are both high due to the coexisting hydrophilic and
hydrophobic regions in the coacervate phase (Fig. 1b). The partition ratios of charged solutes can be tuned
up to 50 times by reversing droplet surface charge.
Figure S5. **a**, Scattering intensity of a DTAB/PTS/β-CD/amylase solution at different temperature (black, red, and blue for 25, 40, and 55 °C, respectively). **b**, Scattering intensity of a DTAB/PTS/CD/amylase solution at 55 °C with black, red, and blue points corresponding to α-CD, β-CD, and γ-CD, respectively.
Figure S6. Synthesis of amylase-grafted polyacrylamide gels.
Figure S7. Protocol to track droplet contours. We first implemented a real-space band-pass filter to the raw image (a) to suppress both small scaled pixel noise and large-scaled image variations. The outcome image (b) retained information of the characteristic droplet size with enhanced signal-to-noise ratio. The rough positions of the droplets were pre-featured by finding the local brightness maximums of (b) using a Gaussian filter. (b) was binarized into (c) by setting the values of pixels that had original brightness larger than a threshold value (usually 90) to 255; while the values of other pixels to 0. For each droplet, we cropped a small square region (30×30 pixels) in (c) that centered at the pre-featured position of it. The boundary of the droplet in d was then featured by applying the chain-code algorithm [http://ccis2k.org/iajit/PDF/vol.6,no.3/7.pdf] to the cropped region. To eliminate false detection, to empirical criteria were set: 1. The perimeter of the detected boundary should be larger than a threshold value (usually 10-20 pixel); 2. The mass center of a droplet determined by averaging the boundary points should not be far away from the pre-featured position (usually less than 10 pixel). Finally, we connected the discrete boundary points into a closed loop by polygon fitting and used the area enclosed by the loop as the size of the droplet.