## **Supporting information**

## Controllable Formation of Bulk Perfluorohexane Nanodroplets by

## **Solvent Exchange**

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The presence of micron droplets was clearly visible at PFH volume ratios of 1/20, 1/100, and 1/200 under the optical microscope, and the size of the micron droplets decreased with decreasing volume ratio. At the volume ratio of 1/1000, no micron droplets were observed under the optical microscope, as shown in Fig. S1.



Fig. S1 Optical microscopic view of the nanodroplet systems

No detectable changes of degassing contributing to the stabilization of nanobubbles were observed in our study, as shown in Fig. S2.



Fig. S2 (A) Effect of degassing on the concentration of nanodroplets; (B) Effect of degassing on the average size of nanodroplets.

It could be seen that the formation of small-size, uniform high-concentration nanodroplets was restricted to Fig. S3, in which a lower propanol concentration and PFH volume ratio were required. In addition, as showed in Fig. S4, the size distribution of nanodroplets would become wide when the propanol concentration was in the range of 20% to 40% but it became uniform at the concentration greater than 40%, the concentration gradually became lower due to the low precipitated nanodroplet nucleus (Fig. S5).



Fig. S3 Blue II triangle area in the phase diagram of PFH nanodroplets.



Fig. S4 Green II triangle area in the phase diagram of PFH nanodroplets.



Fig. S5 Black III cross area in the phase diagram of PFH nanodroplets.

We investigated the effect of the drop acceleration rate of PFH propanol solution and stirring time on the properties of nanodroplets. Take the system of  $5\mu$ L PFH and 10% propanol as an example, the results indicated that the concentration of nanodroplets decreases with the decrease of the drop acceleration rate of PFH propanol solution, and the average sizes show a trend of first increasing and then decreasing. Stirring helps the formation of nanodroplets while too long time (such as longer than 10 s) will instead decrease the concentration of nanodroplets. But stirring has little effect on the size of nanodroplets, as depicted in Fig. S6.



Fig. S6 (A) Nanodroplets concentration and average size plotted against vortex time; (B) Nanodroplets concentration and average size plotted against drop acceleration rate of PFH propanol solution.