Supporting Information

## **Emulsions by Miscible Solvents: Origin for Anti-solvent Crystallization**

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## **Supporting figures**



**Figure R1**. Small-angle X-ray scattering (SAXS) data showing q value corresponding to *ca*. 6.8 nm for the solution of toluene (1 ml) and ethanol (0.1 ml). ( $\lambda$ =1.24 Å)



**Figure S2**. Raw data of dynamic light scattering (DLS) results showing the emulsion particles' size (above) and after 17 h (below) in toluene/ethanol (1/0.1 ml) mixed solvents.



**Figure S3**. Time-dependent DLS data measured for an hour at every ten minutes for toluene (1 ml) and ethanol (0.4 ml) mixed solvents.



**Figure S4.** Phase Graph of quantity of anti-solvent added *vs.* solution concentration of  $C_{70}$ . a and b. although anti-solvent was added, no crystallization occurs, indicating that the does not reach to supersaturation, staying in a undersaturation state. c. Saturation point where nucleation occurs., when more anti-solvent is added beyond point c, the whole solution reaches to supersaturation state (d) and starts to solidify to make the solution in a new equilibrium state.<sup>S1</sup>



**Figure S5.** Effect of pre-mixed toluene/ethanol solvent. Photograph of when pre-mixed solvent was used (left) and when solvents were sequentially added (right).



**Figure S6.** Dynamic light scattering results for average size of the emulsions particles in (b) acetone/toluene and (c) methanol/toluene mixed solvent systems.



**Figure S7**. Optical microscopy images of Methylene blue crystals showing the polarity effect of poor solvent. n-hexane (nonpolar) and acetone (polar) poor solvents were added into Methylene blue/ethanol solution. (5 mg/ml)



**Figure S8**. Raw data of dynamic light scattering (DLS) results showing the emulsion particles' size in ethanol/n-hexane (1/0.1 ml) mixed solvents.

## Reference

S1. Coquerel, G. Crystallization of molecular systems from solution: phase diagrams, supersaturation and other basic concepts. *Chem. Soc. Rev.*, **2014**, *43*, 2286-2300.