

## Supporting Information

### Shedding Light on the Formation and Stability of Mesosttructures in Ternary “Ouzo” Mixtures

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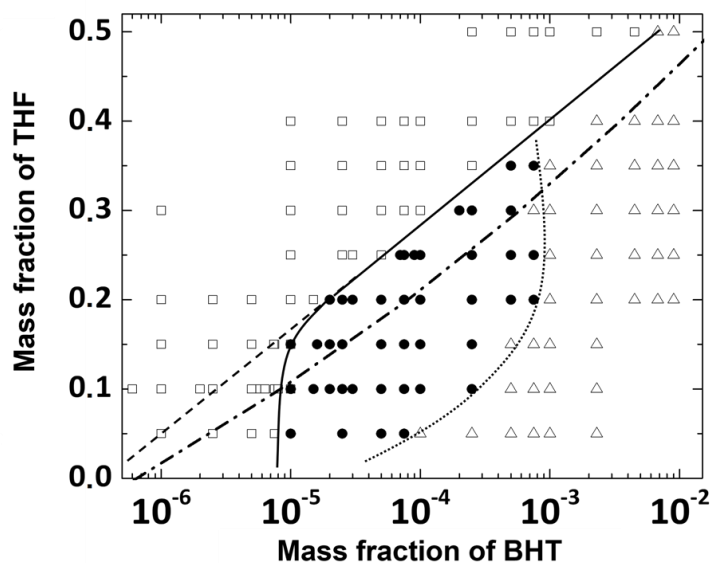


Figure SI-1: Semi-Log representation of the phase diagram water/THF/BHT determined by visual observation: ( $\square$ ) limpid samples; ( $\bullet$ ) cloudy samples; ( $\Delta$ ) biphasic samples. (—) cloudiness curve, (- - -) linear extrapolation of the cloudiness curve, (.....) boundary between cloudy and macroscopically biphasic samples, (- · - · -) binodal curve calculated by COSMO-RS.

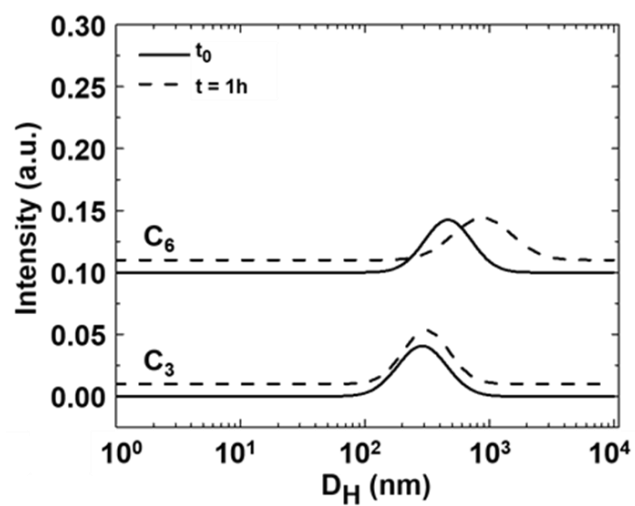


Figure SI-2: Size histogram in intensity from DLS analysis for compositions  $c_3$  and  $c_6$ . Full line (—): initial time; dashed line (- -) after 1 hour.

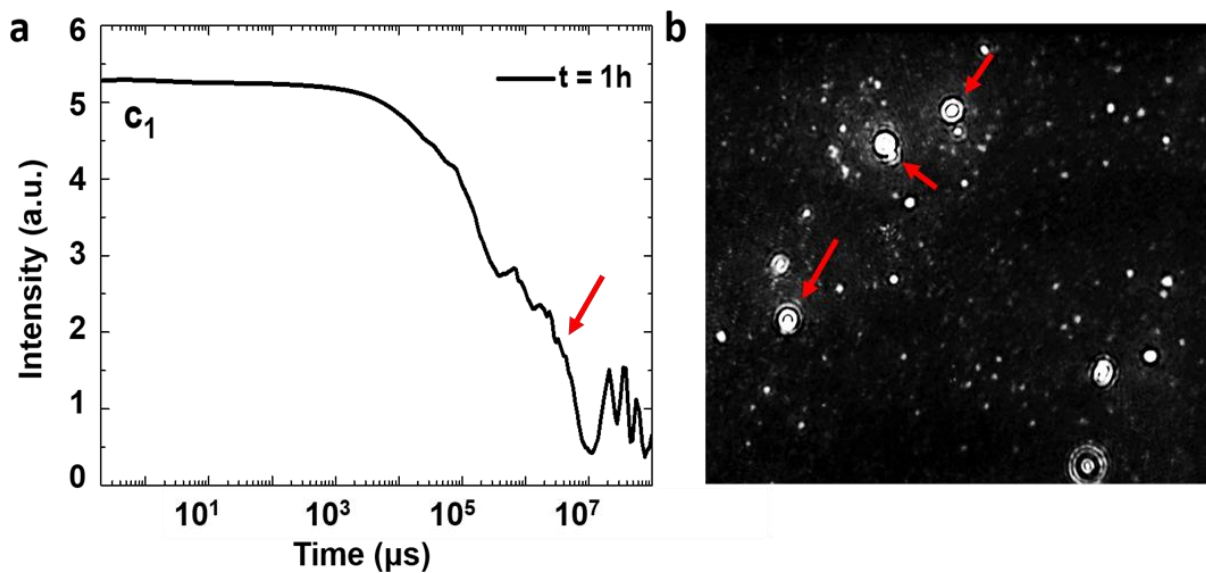


Figure SI-3: Sample  $c_1$  ( $\Phi_{\text{BHT}} = 2.5 \cdot 10^{-6}$ ,  $\Phi_{\text{THF}} = 0.2$ ): Correlogram from DLS analysis (a) and snapshot of the illuminated cell during NTA analysis (b), showing the scattering from larger droplets.

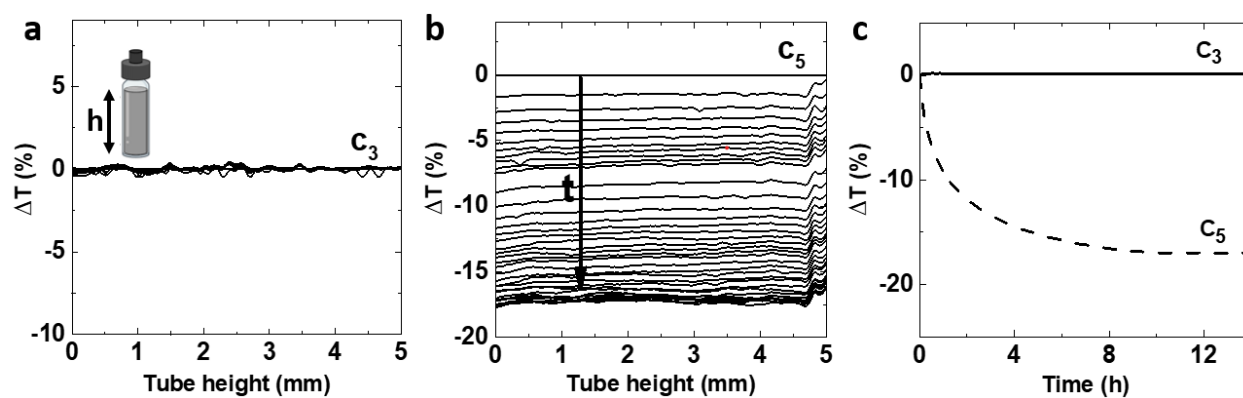


Figure SI-4: SMLS stability analysis of samples along the composition line  $\Phi_{\text{THF}} = 0.2$  (a) transmission of the sample  $c_3$  along tube height for different times, relative to the transmission at  $t=0$ ; (b) idem for sample  $c_5$ ; (c) Time evolution of their relative transmission measured at mid-height.

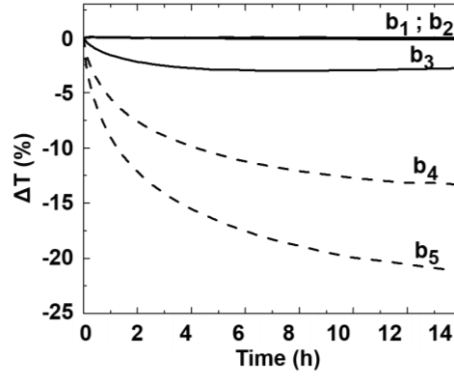


Figure SI-5: Relative transmission measured at mid-height for samples along the composition lines  $\Phi_{THF} = 0.15$  (samples  $b_n$ ). Full line (—): limpid samples; dashed line (---): cloudy samples.

*Remark on the influence of the mixing mode:* Some authors suggested that because the Ouzo effect is considered as a spontaneous emulsification, it requires no mixing and mixing modes have no effect on the final size distribution.<sup>33</sup> However, this is not true. The nucleation conditions in the Ouzo domain are sensitive to mixing conditions.<sup>14</sup> A rapid mixing rate (compared to nucleation rate) favors homogeneous nucleation. Therefore, we found it necessary to check if habits of different operators regarding mixing could influence our results. Two types of mixing typical of standard laboratory conditions were compared. In the first case (“manual mixing”), the vial was gently turned up-side down 3 times. In the second case, it was mixed strongly using a vortex for 10 seconds. Figure SI- 3 shows the stability analysis of samples  $a_0$  and  $a_2$  for both mixing conditions. As expected, in the thermodynamically stable domain ( $a_0$ ), the samples show no evolution, for both mixing methods. For sample  $a_2$  (in the metastable domain), in both cases the sample evolves, although with a different dynamic. In conclusion, the location of the binodal as determined by SMLS does not seem to be influenced by the mode of mixing.

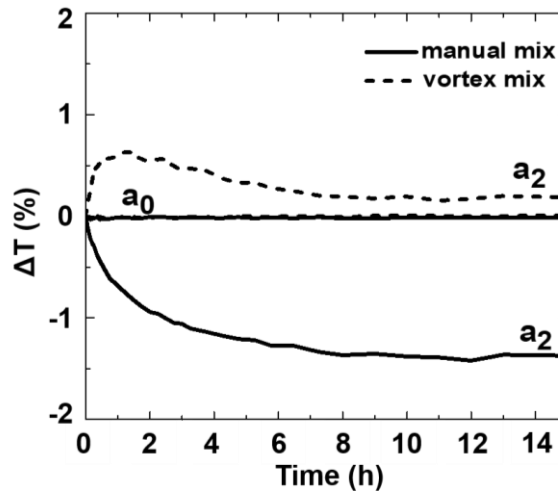


Figure SI-6: Influence of the mixing mode on the kinetics of the sample measured via SMLS.

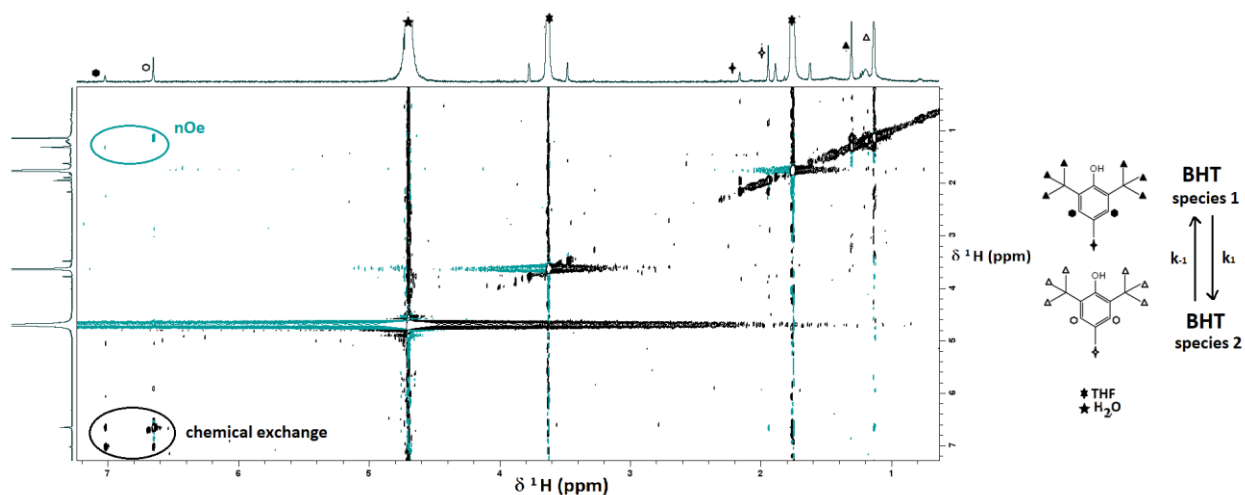


Figure SI-7: 2D  $^1\text{H}$  NOESY NMR spectrum of BHT for sample  $a_6$  ( $\Phi_{\text{THF}d8} = 0.1$  and  $\Phi_{\text{BHT}} = 2.5 \cdot 10^{-5}$ ). The resonances of the BHT protons are identified by symbols in accordance with their chemical equivalence as indicated on the molecules drawn on the right of the spectra.

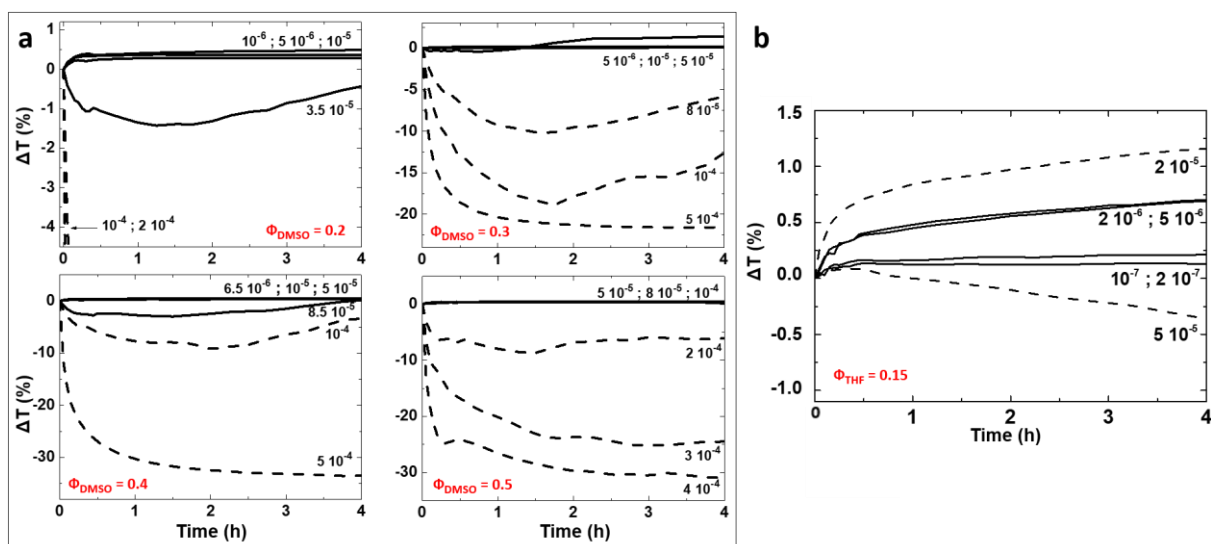


Figure SI-8: Relative transmissions measured at mid-height by SMLS of the samples from the systems (a) water/DMSO/limonene along the composition lines  $\Phi_{\text{DMSO}} = 0.2, 0.3, 0.4, 0.5$  and (b) water/THF/ $\alpha$ -tocopherol along the composition line  $\Phi_{\text{THF}} = 0.15$ . Full line (—): limpid samples; dashed line (---): cloudy samples. The SMLS analysis was performed during 14 hours as previously but the graphs show a zoom over the first 4 hours of the experiment.

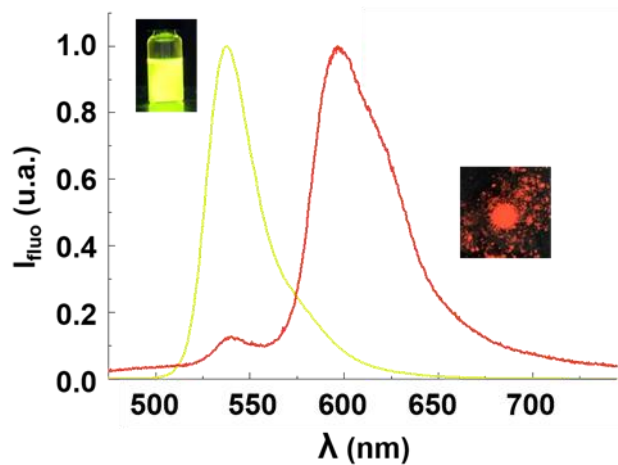


Figure SI-9: Reference emission spectra of the pristine BODIPY dye (arbitrary units); red: solid state (powder); yellow: dissolved in THF.

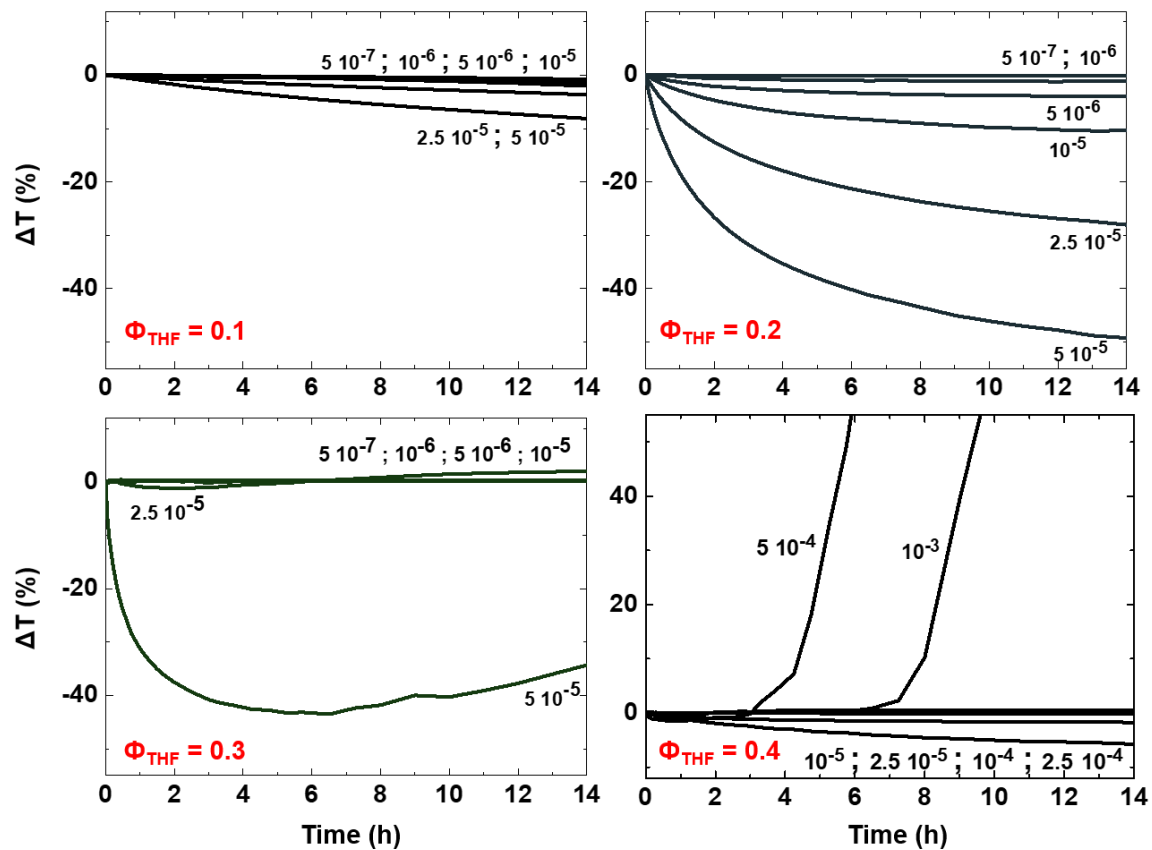


Figure SI-10: SMLS analysis of samples water/THF/BODIPY, along composition lines  $\Phi_{\text{THF}} = 0.1$ ;  $0.2$ ;  $0.3$  and  $0.4$ . ( $\Phi_{\text{BODIPY}}$  as indicated on graphs).

