Tuning aggregation-induced emission nanoparticle properties under thin film formation

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#### **Supplementary information**

## **Supplementary S1**

The FL property of TPE particles is sensitive to the water/THF fraction. As explained in the context of manuscript, for water fraction larger than 80%, TPE particles are emissive with a sharp increase at 95-97% water content. Therefore, evaporation of THF during rotation of the VFD tube results in increase of water fraction that affect the associated FL property. To minimize the effect of THF evaporation the following acts and measurement were considered. **S1-1: Measurement of temperature.** VFD tube was filled with water and change in temperature was measured as a function of rotation speed at different time intervals of 5 min. temperature was measured by two different methods:

1- A sensitive thermocouple was placed inside the VDF tube and connected to an indicator. It was found that after 30 min rotation (steps of 5 min from 4000 RPM to 8000 RPM) temperature raised to approximately 33°C.



4000 RPM, t= 0 min

4000 RPM, t= 3 min

2- An infrared camera was used to measure the temperature at different points of the tube. The highest tube temperature that was recorded close to the bottom of the tube was 29.6°C at 8000 RPM. The highest measured temperature for the entire VFD was 37.7°C at the electric motor.



Based on these measurements, the average temperature change of the VFD tube at different rotation speed was as follow



As seen, the highest recorded temperature was well below boiling temperature of water and THF. It is unlikely that evaporation of THF occurred because of temperature rise.

**S1-2: Accurate physical sealing of the mixing environment.** A cap was designed to seal the VFD tube properly. An accurate hole was placed at the centre of the cap for injection of TPE-THF solution into the rotating water. The gap between the cap hole and injection feed was less than 100 μm.



**S1-3:** In situ measurement of the FL property: The FL property of TPE particles was measured after preparation (30 s of rotation) is situ using a modular USB spectrophotometer (Ocean optics, USA), fibre optics and OceanView software. This allows real-time acquisition and analysis.



**S1-4: Negligible change in water fraction was found for VFD- driven particles:** NMR was used to check the possible loss of THF during rotation. Two different water fractions (90% and 40%) was evaluated. The loss of THF molar fraction was found less than 5%.







NMR results for WF=90%









**Supplementary S2-** Change in relative intensity for TPE particles at different water fractions. Increase in rotation speed results in increase of relative FL intensity.







**Supplementary S3-** Change in FL spectra maxima versus water fraction at constant rotation speeds. For less than 40% water fraction, increase in rotation speed has no impact on the FL property of TPE particles. When water fraction set to 40-60%, increase in rotation speed results in higher emission for TPE particles. In general, at a constant rotation speed, increase in water fraction leads to higher FL property.



**Supplementary S4-** Size distribution by intensity for traditionally prepared TPE particles at 0 RPM and different water fractions.



**Supplementary S5-** The captured images by a fluorescent microscope at different rotation speeds were consistent with what we observed for reduction of TPE particle size. To prepare these images, we placed a drop of solution containing TPE with water fraction of 80% in a cavity of slide microscope and covered by a coverslip. Since we didn't use dilute solution the agglomeration of TPE particles hindered their actual size; however, we saw a similar trends where the size of agglomerates was reduced when rotation speed increased.





I: rotation speed = 0 RPM

II: rotation speed = 2000 RPM

III: rotation speed = 4000 RPM

**Supplementary S6-** Size distribution by intensity for VFD-driven TPE particles at different rotation speeds. Water fraction was set to 90% for all samples and as seen increase in rotation speeds leads to creation of extremely lower particle.



**Supplementary S7-** Size distribution by intensity for VFD-driven TPE particles at different rotation speeds. Water fraction was set to 60% for all samples and as seen increase in rotation speeds leads to formation of lower particle.



**Supplementary S8-** Size distribution by number for traditionally prepared compared to VFDdriven (4000 RPM) TPE particles at 60% water fraction. Increase in rotation speed at constant water fraction leads to formation of smaller TPE particle.



**Supplementary S9-** Size distribution by number for traditionally prepared compared to VFDdriven (2000 RPM) TPE particles at 70% water fraction. Increase in rotation speed at constant water fraction leads to formation of smaller TPE particle.



**Supplementary S10-** Size distribution by number for VFD-driven TPE particles prepared at 95% water fraction and two different rotation speed of 1000 and 4000 RPM. Increase in rotation speed at constant high-water fraction leads to formation of extremely smaller TPE particle.



**Supplementary S11-** Size distribution by number for TPE nanoparticles as a function of water fraction at different constant rotation speeds. At a constant rotation speed increase in water fraction leads to reduction of particle size.



**Supplementary S12-** Absorbance, integrated emission intensity, quantum yield measurement, increase of quantum yield as a function of rotation speed for THF-water fraction = 60%, 80% and 90\%, as well as the UV-vis absorbance and FL intensity spectrum for the reference material (QS) and sample prepared at water/THF= 90% and 4000 RPM.

# Simple Reads Report- Absorbance

Read	Abs	nm	
Zero	(0.0791)	500.0	
QS	0.0695	350.0	
80-0RPM	0.0749	350.0	
80-1000RPM	0.0939	350.0	
80-2000RPM	0.0998	350.0	
80-3000RPM	0.0724	350.0	
90-0RPM	0.0871	350.0	
90-4000RPM	0.0786	350.0	
60-4000RPM	0.0949	350.0	

## Integrated emission intensity

Sample	Area under the curve		
	(IEI)		
QS (reference)	13821		
80-0RPM	266.57		
80-1000RPM	1329.3		
80-2000RPM	5031.9		
80-3000RPM	5233.9		
90-0RPM	4841.8		
90-4000RPM	12148		
60-4000RPM	4064.1		

# Quantum yield

Sample	A <sub>r</sub>	IEI <sub>r</sub>	φ <sub>r</sub>	A <sub>s</sub>	IEIs	φs
80-0RPM	0.0695	13821	0.546	0.0749	266.57	0.97%
80-1000RPM	0.0695	13821	0.546	0.0939	1329.3	3.88%
80-2000RPM	0.0695	13821	0.546	0.998	5031.9	13.84%
80-3000RPM	0.0695	13821	0.546	0.0724	5233.9	19.97%
90-0RPM	0.0695	13821	0.546	0.0871	4841.8	15.29%
90-4000RPM	0.0695	13821	0.546	0.0786	12148	42.43%
60-4000 RPM	0.0695	13821	0.546	0.0949	4064.1	11.75%
60-0RPM	0.0695	13821	0.546	-	0	0%





## Supplementary S13 - Evaluation of crystallinity of TPE nanoparticles

To identify whether VFD-mediated TPE nanoparticles are in crystalline state or not, a polarizing microscope (Olympus, BH-2 series) with a blue light filter (KB-4) was used and microscopic images were captured using a colour camera (Olympus, DP20). To prepare samples, a drop of solution from VFD-mediated TPE nanoparticles, prepared at WF= 80% and 90% at 3000 RPM, were placed on microscope slides. The microscope slides were placed in room temperature for evaporation of media (water and THF).

Once the polariser and analyser filters were aligned a dark background was produced indicating the analyser oriented 90° to the polariser. During imaging, any birefringent structure was displayed as bright or colourful features on the dark background. Our microscopic evaluation revealed that TPE nanoparticles are in the crystalline state.



Evaluation of Polariser and analyser filters, the blank sample (just a microscope slide) for (a0 non-aligned and (b) aligned filters. The dark background shows that the analyser was oriented  $90^{\circ}$  to the polariser. Scale bars=  $30 \,\mu$ m.



Images of TPE nanoparticles using a polarizing microscope prepared at 3000 RPM rotational speed at WF = (a) 80% and (b) 90%. Scale bars=  $30 \mu m$ .



Blue shift for VFD-mediated TPE nanoparticles prepared at 1000 (purple) and 3000 (black) RPM at THF-water fraction = 60%



**Supplementary S14** – Stability of VFD-mediated TPE nanoparticles measured at 3000 RPM and WF= 80%.

**Supplementary S15-** Simplified theoretical modelling for estimation of resultant forces applied to the TPE-THF drop by rotating water

To calculate the balance of forces, consider a single drop of TPE-THF solution within the VFD tube, as schematically presented:



R is the radius of VFD tube,  $\theta$  is tilt angle,  $\omega$  is rotation speed and r is the radius of TPE-THF drop.

It was well discussed that there are a number of forces that operate within the VFD including gravity, the centripetal force, electrostatic interaction between tube and liquid, surface tension, liquid viscosity and vibrations. While derivation of a full force- balance equation may lead to better understanding of micro-mixing and flow patterns in theory; it is believed that presenting a simple equation is more helpful for clarifying the mechanism behind our observations, in practice. More importantly, the assumptions for simplification in our case are unlikely to

impact the final results significantly. For example, in the absence of electric charges (ions) the effect of forces driven by electrostatic interactions (repulsion and attraction) are negligible. Also the effect of surface tension is recognised as being not significant for high rotation speeds.

Therefore, the effective forces exerted on a small drop of TPE-THF solution are gravity (including buoyancy), the centripetal and pressure forces. The projection of these forces in radial (r) and tangential (t) directions are known as lift and drag forces, respectively.



Therefore, the magnitude of the resultant force exerted to the drop can be calculated by:

$$R = \sqrt{\left(\sum F_r\right)^2 + \left(\sum F_\theta\right)^2} = \sqrt{F_{lift}^2 + F_{drag}^2}$$

To formulate the pressure force, change in pressure in radial direction that results from the rotation of water in the tube is:

$$dp(A) = mr\omega^{2} = \rho Vr\omega^{2} = \rho A.dr\omega^{2}$$
$$dp = \rho.dr\omega^{2}$$
$$= \int_{0}^{p} dp = \int_{0}^{r} \rho \omega^{2} dr = \rho \omega^{2} \int_{0}^{r} dr = \frac{\rho \omega^{2}}{2} r^{2}$$
$$p = \frac{\rho \omega^{2}}{2} r^{2}_{33}$$

р

Therefore, the pressure force exerted to the small drop is:

$$F_{pressure} = \frac{1}{2} \times (4\pi r^2) \times \frac{\rho \omega^2}{2} r^2 = \rho \pi r^4 \omega^2$$

Gravity force also can be estimated as:

$$F_{gravity} = \frac{4}{3} r^3 (\rho_d - \rho_w) g$$

Where  $\rho_d$  and  $\rho_w$  are density of THF and water, respectively.

To formulate drag and lift force:

$$F_{drag} = F_{gravity} \cdot Sin\theta = \frac{4}{3}\pi r^3 (\rho_d - \rho_w)g.sin\theta$$

$$F_{lift} = F_{pressure} - F_{gravity}Cos\theta = \rho\pi r^4 \omega^2 - \frac{4}{3}\pi r^3 (\rho_d - \rho_w)g.Cos\theta$$

$$R = \sqrt{(\frac{4}{3}\pi r^3 (\rho_d - \rho_w)g.sin\theta)^2 + (\rho\pi r^4 \omega^2 - \frac{4}{3}\pi r^3 (\rho_d - \rho_w)g.Cos\theta)^2}$$

As obvious, the resultant force depends on rotation speed and size of the drop; however, for any drop with individual diameter, the resultant force rises as the rotation speed increases. For drop with radius = 2mm:



For drop with radius = 3mm:



For drop with radius = 4mm:



**Supplementary S16**-The superimposed image of *Euglena gracilis* captured under excitation at 365 (to highlight the agglomeration of TPE aggregates) and 470 nm (Euglena auto fluorescence).



# The Structure of single-celled Euglena

