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Supplementary information

Vortex fluidic enabling and significantly boosting light intensity of graphene oxide with aggregation induced emission luminogen

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Experimental

Materials and reagents

Single-layer graphene oxide which can be dispersed in water (CAS No.: 7782-42-5) was purchased from ACS Materials, Australia. Dimethyl sulfoxide (DMSO) was purchased from Sigma-Aldrich, Australia. TPE-2BA was purchased from AIEgen Biotech Co., Ltd, Hong Kong, China.

Sample preparation

A stock solution of TPE-2BA in DMSO with a concentration of 10 mM was prepared by dissolving 0.105 g (250 µmol) of TPE-2BA in 25 mL DMSO. The solution was stored in a refrigerator at 4 °C for further use. GO solutions (in water) were prepared at different concentrations (0.001- 0.007 mg/mL).

Preparation of TPE-2BA and GO/TPE-2BA

Aliquots of the stock solution were transferred to 5 mL volumetric flasks. After appropriate amounts of DMSO were added, the final aliquot solutions were added to water dropwise and under stirring to furnish 100 µM solutions with different water fractions (50-90%). To prepare the GO/TPE-2BA complex, TPE-2BA solution in DMSO (100 µM) was added to the GO solution under constant stirring at different pre-set WFs (the ratio of TPE-2BA in DMSO to GO in water was set to achieve desirable WF).

Preparation of GO/TPE-2BA using VFD

2400 mL of GO solution (in water) was added to the VFD tube and the rotation speeds were set to 1000 to 5000 RPM (step 1000 RPM). After 5 minutes and at each rotation speed, 600 mL of TPE-2BA solution (in DMSO) was injected into the high-speed rotating tube, so the water fraction was selected to 80%.

Fluorescence measurement

The FL emission intensities were taken for samples prepared at different water fractions and GO concentrations using a spectrophotometer (Cary Eclipse, Agilent Technologies, Australia). The excitation wavelength was set at 310 nm.

Measurement of stability

The stability of the FL property for GO/TPE-2BA at WF=80% was identified using a spectrophotometer (Cary Eclipse, Agilent Technologies, Australia). The FL intensity at an excitation wavelength of 310 nm was recorded for as-prepared samples and at different time points.

Particle size measurement

The size of the TPE-2BA particles was measured using a dynamic light scattering method, in a Zetasizer (Malvern, US). All samples were diluted before measurement by adding one drop of a solution containing particles to 2 mL of water.

High-speed camera imaging

A high-speed camera (V1212, DANTEC Dynamics, Australia) with 35 mm lens was used to capture transient phenomena at 12,600 fps within the VFD tube upon injection of the TPE-2BA solution into the GO solution.

Atomic force microscopy

AFM images were acquired using a Bruker Dimension FastScan AFM with Nanoscope V controller, and Nanoscope control software (version 8.15). AFM images were acquired using peakforce tapping mode with all parameters including set-point, scan rate and feedback gains adjusted to optimize image quality and minimize imaging force. Images were acquired using ScanAsyst-air probes (Bruker) with nominal spring constant of 0.4 N m^{-1} and nominal tip diameter of 4 nm.

Fluorescence quantum yield measurement.

The FL emission intensities were taken for samples (TPE-2BA and GO/TPE-2BA) prepared at wf= 80% and different rotation speeds. The excitation wavelength was set at 310 nm. The area under emission peaks (integrated emission intensity) was calculated by using the spectrophotometer software (Cary Eclipse, Agilent Technologies). The absorbance of the samples at 310 nm was measured using UV-vis spectrophotometer (Cary 60, Agilent Technologies). Quinine sulphate (QS) was used as a reference with known quantum yield and refractive index values of 0.546 and 1.346, respectively. During measurement, in order to minimize the effect of the re-absorption, absorbance in the 10 mm cuvette was adjusted below 0.1. The absorbance for QS was measured as 0.0695. The refractive index for water and DMSO is 1.333 and 1.404 respectively. Therefore, the refractive index for the sample was averaged and estimated at 1.368. However, for the calculation of quantum yield, the ratio of refractive index for sample and reference was approximated as 1 (1.368/1.346 = 1.016).

Quantum yield for samples was calculated using the following equation:

$$\emptyset_s = \emptyset_r \times \frac{A_r}{A_s} \times \frac{IEI_s}{IEI_r} \times \frac{n_s^2}{n_r^2}$$

where ϕ, A, IEI and n represent quantum yield, absorbance, integrated emission intensity, and refractive index, respectively. S and r were used to identify sample and reference material (Quinine sulphate, QS).

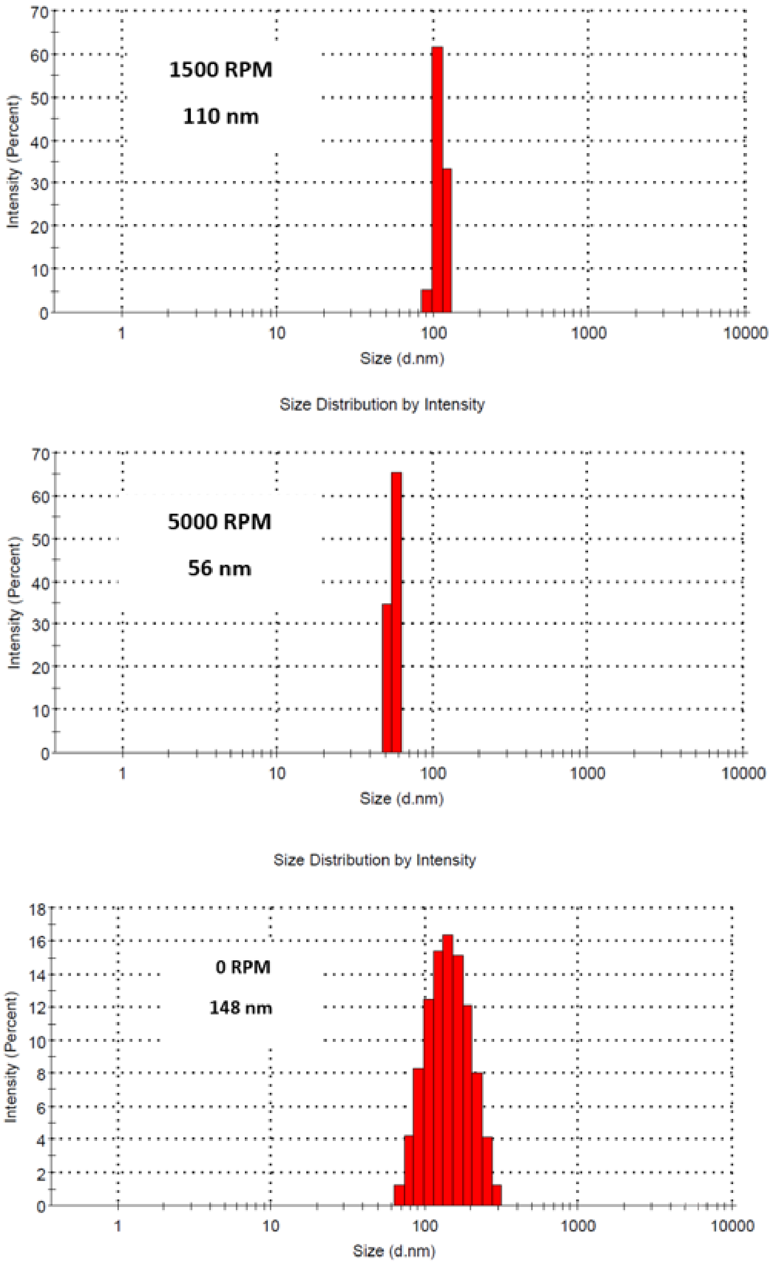


Figure S1. Size distribution for TPE-2BA particles at WF=80% and two different rotational speeds of 1500 and 5000 RPM.

Table S1. Quantum yield measurement

Sample	WF (%)	Rotation (RPM)	As	IEIs	Ar/As	IEIs/IEIr	QY (%)
AIE	80	0	0.053	6460.7	1.492453	0.146904	11.9
AIE/GO	80	0	0.0398	15360	1.987437	0.349258	37.9
AIE/GO	80	1500	0.0401	32501	1.972569	0.739012	79.6

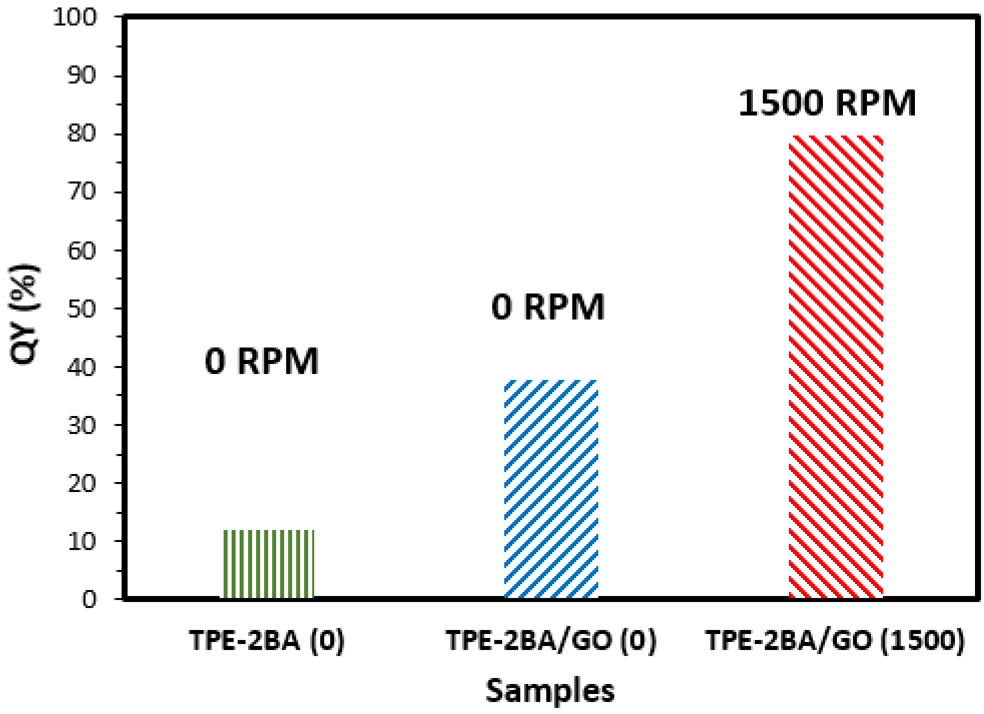
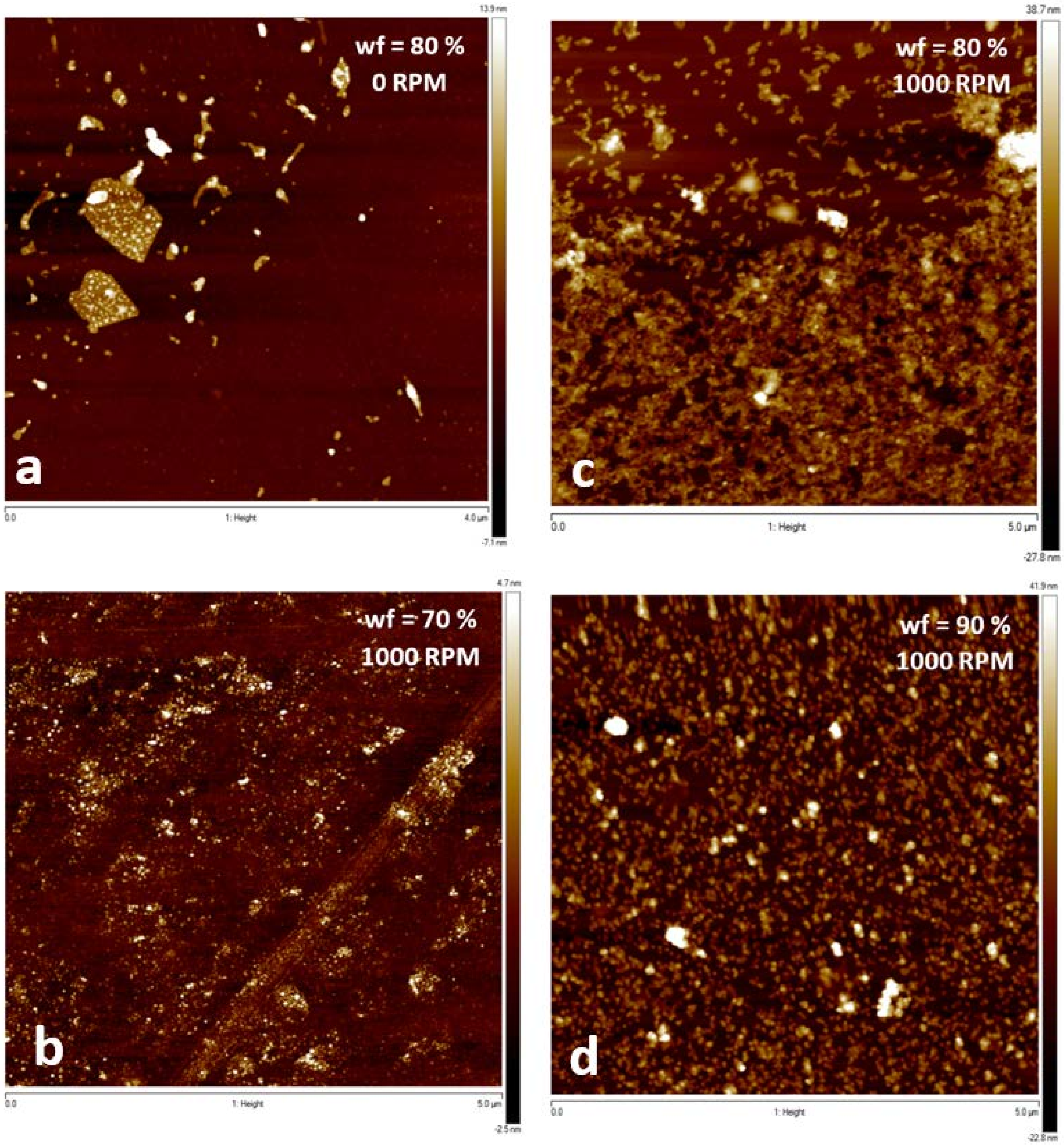


Figure S2- Quantum yield measurement for TPE-2BA and TPE-2BA/GO at 0 and 1500 RPM.

The proposed mechanism, along with the FL properties of the GO/TPE-2BA complexes were also consistent with the AFM images captured from GO/TPE-2BA complexes to support the proposed mechanistic drawings. We found a similar height profile (≈ 40 nm) for both samples prepared at 1000 RPM and different wf = 80 and 90%. However, for wf = 80% average particle size (Measured by AFM) were approximately 60 nm with decreasing to 50 nm for wf= 90%. This observation was consistent with the fluorescent results revealing smaller relative intensities for wf = 90% compared to that was prepared in 80%. Referring to the AIE curve of TPE-2BA (Figure 1a – main text), it is apparent that the relative fluorescent intensity at wf= 90% was smaller, compared to that of prepared at wf = 80%. It seems that TPE-2BA/GO that was prepared at wf = 90% created a larger surface than that of prepared at wf = 80%; however, bigger TPE-2BA aggregates at wf = 90% leading to a lower brightness.

We also included an AFM image of TPE-2BA/GO that was prepared at wf= 80% and 5000 RPM to further support our findings. It was apparent that the application of high shear stress (5000 RPM) compared to low shear stress (1000 RPM) resulted in more districted areas rather than a uniform film with the height of the samples at high shear stress was > 50 nm. In contrast, for TPE-2BA/GO that was prepared at the same wf (80%) but lower shear stress (1000 RPM) the height was 40 nm. This observation may identify that under high shear stress GO sheets encapsulated TPE-2BA aggregates and creating isolated regions. The results drawn from AFM images are consistent with our schematic drawings to describe the possible mechanism for GO affecting the fluorescence property of TPE-2BA/GO complex.



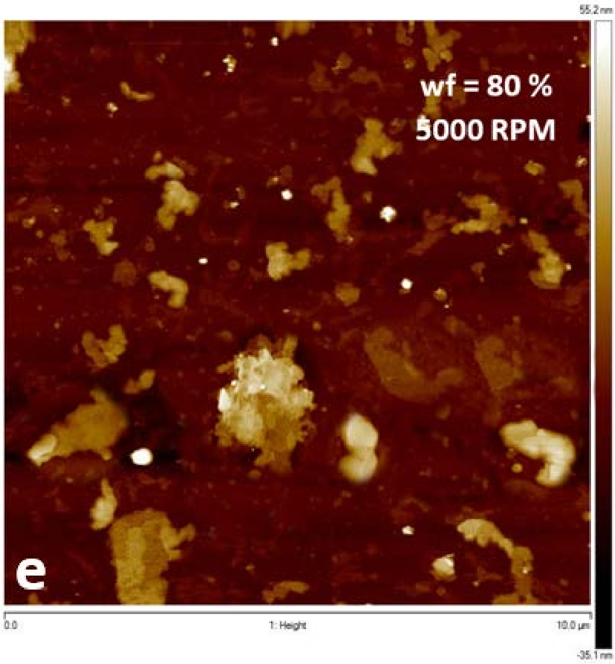


Figure S3. AFM images captured from GO/TPE-2BA complexes prepared by (a) batch production (RPM = 0, wf = 80%), using a VFD at 1000 RPM with wfs = (b) 70%, (c) 80% and (d) 90% and (e) using a VFD at 5000 RPM with wf = 80%.