

Supporting Information

Hyper-branched polymer tunes size and enhances fluorescent properties of aggregation-induced emission nanoparticles

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S1. Experimental section

Materials: PVA (Mowiol ® 28-99, CAS No: 9002-89-5, molecular weight 145,000 and degree of hydrolysis > 99%) and dimethyl sulfoxide (DMSO), hyper-branched polymer (bis-MPA polyester-64-hydroxyl, generation 4, CAS No: 326794-48-3) and creatinine (CAS No: 60-27-5) were purchased from Sigma-Aldrich, Australia. TPE-2BA was purchased from AIEgen Biotechnolog, 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. 1.465 gr of hyper-branched polymer was dissolved in 200 mL DMSO to prepare hyper-branched polymer solution (1 mM).

Preparation of TPE-2BA and AIE-HBP: 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 50 µM solutions with different water fractions (20-90%). To prepare AIE hyper-branched polymer TPE-2BA/DMSO solution was added to the hyper-branched polymer (HBP) /DMSO solution under constant stirring. Then water was added to the vigorously shaken final solution at different pre-set WFs, while the concentration of TPE-2BA (50 µM) and HBP (1 mM) remained constant.

Preparation of AIE-HBP using VFD: 2700 mL of water was added to the VFD tube and the rotation speeds were set to 1000 to 5000 RPM (step 1000 RPM). At each rotation speed 300 mL of TPE-2BA (AIE) in DMSO was injected into the high speed rotating tube, so the water fraction was selected to 90%.

Hydrogel preparation: PVA solution (6% w/w) was prepared by dissolving PVA powder in water. AIE-HBP at WF=90% was prepared as explained above. A solution containing 10% AIE-HBP and 90% PVA solution(6%) was prepared by constant stirring at room temperature for 30 minutes. Hydrogel films were prepared by a drop-casting method with a thickness of 1 mm. Final films were cut to rectangle shapes with 5 mm × 20 mm dimensions.

Fluorescence quantum yield measurement. The FL emission intensities were taken for samples prepared at different water fractions. 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:

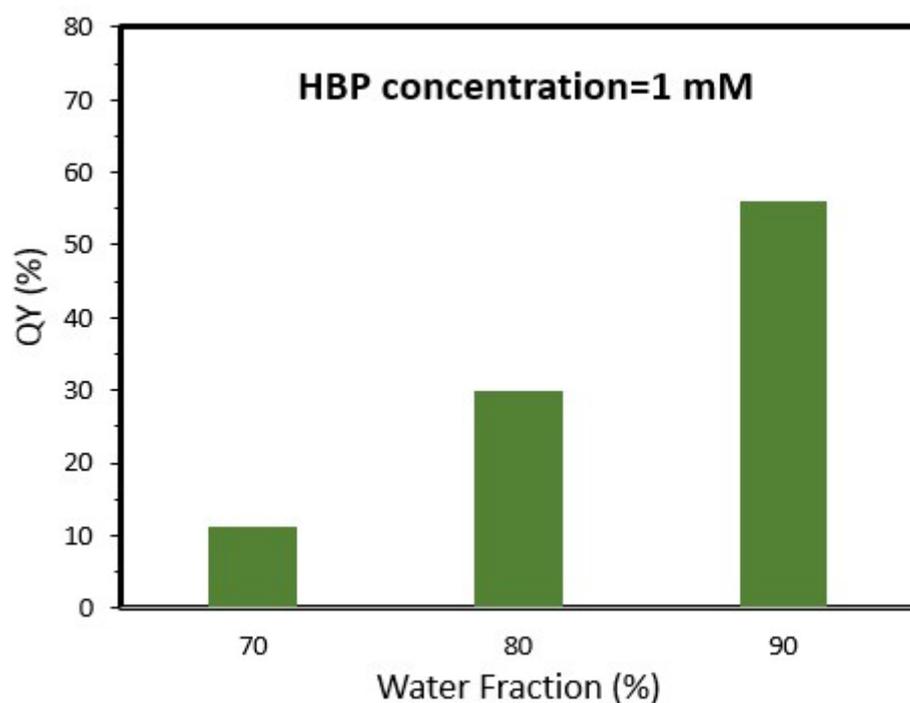
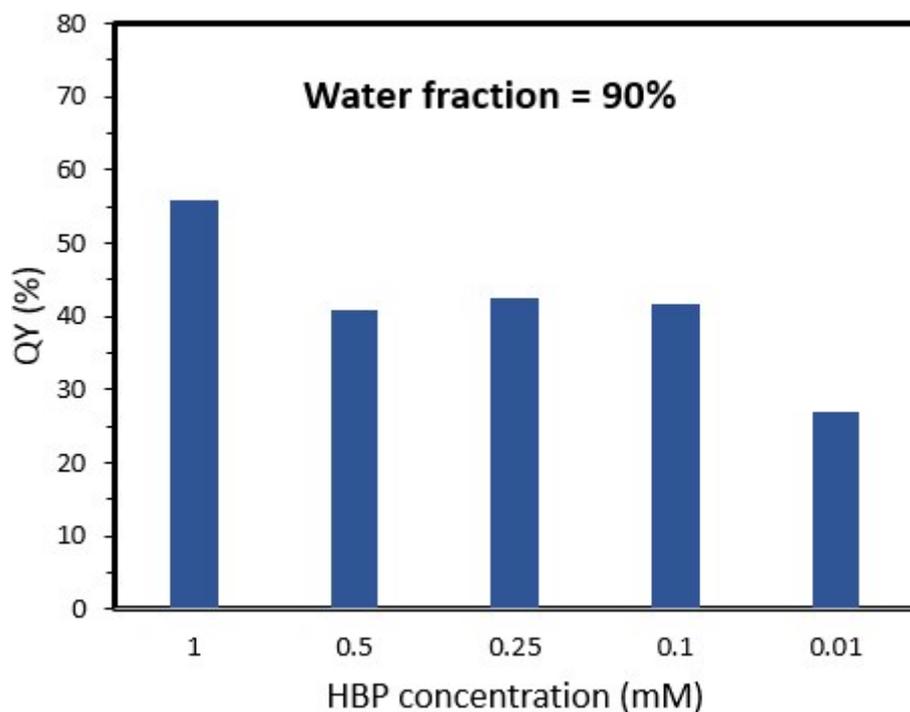
$$\phi_s = \phi_r \times \frac{A_r}{A_s} \times \frac{IEI_s}{IEI_r} \times \frac{n_s^2}{n_r^2}$$

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).

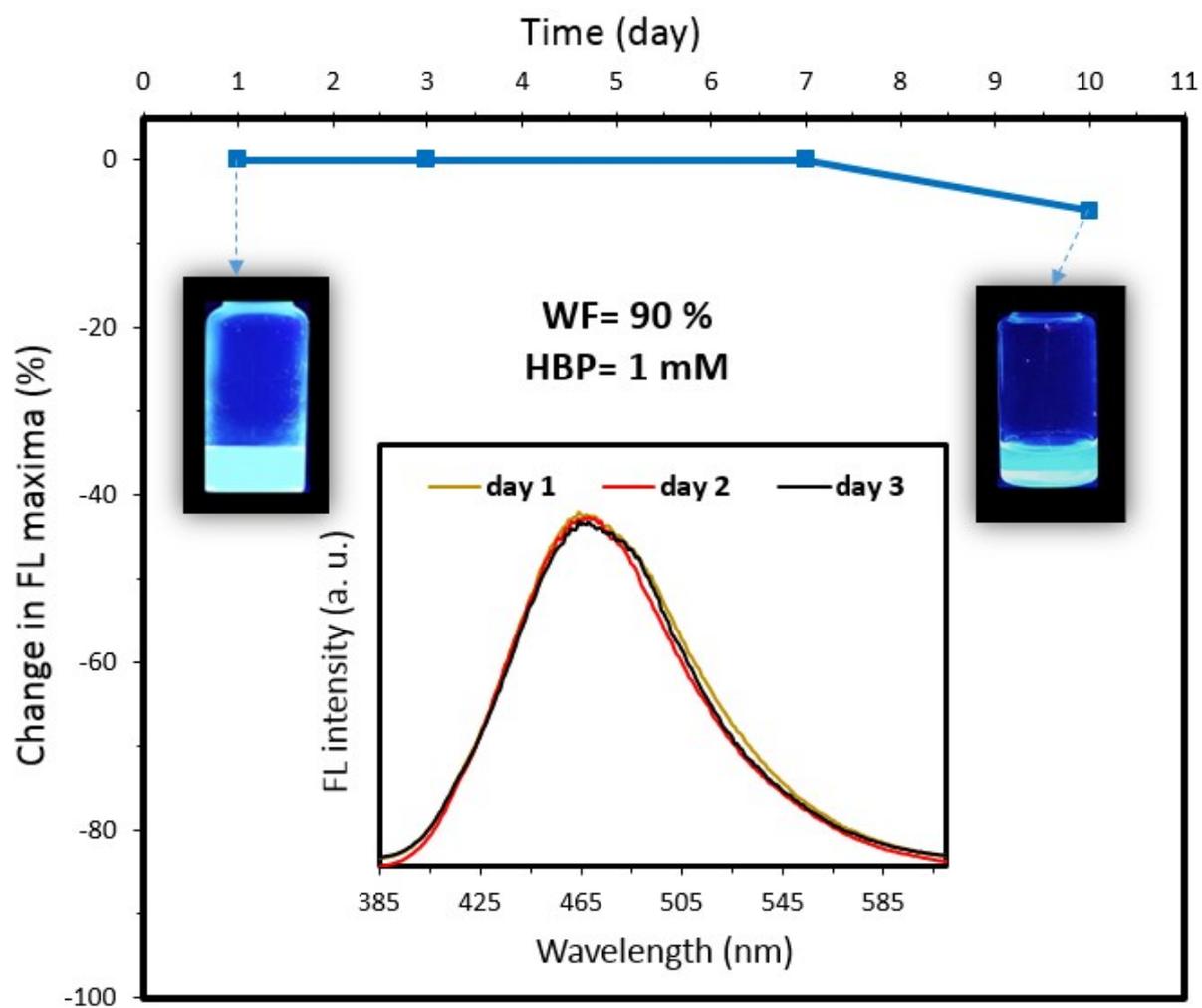
Measurement of stability: The stability of the FL property for AIE-HBP at WF=90% was identified using a spectrophotometer. The FL intensity at an excitation wavelength of 310 nm was recorded for as-prepared samples and at different time points.

Particle size measurement: The size of the TPE-2BA and AIE-HBP particles was measured using a dynamic light scattering method, in a Malvern Zetasizer. All samples were diluted before measurement by adding one drop of a solution containing particles to 2 ml of water.

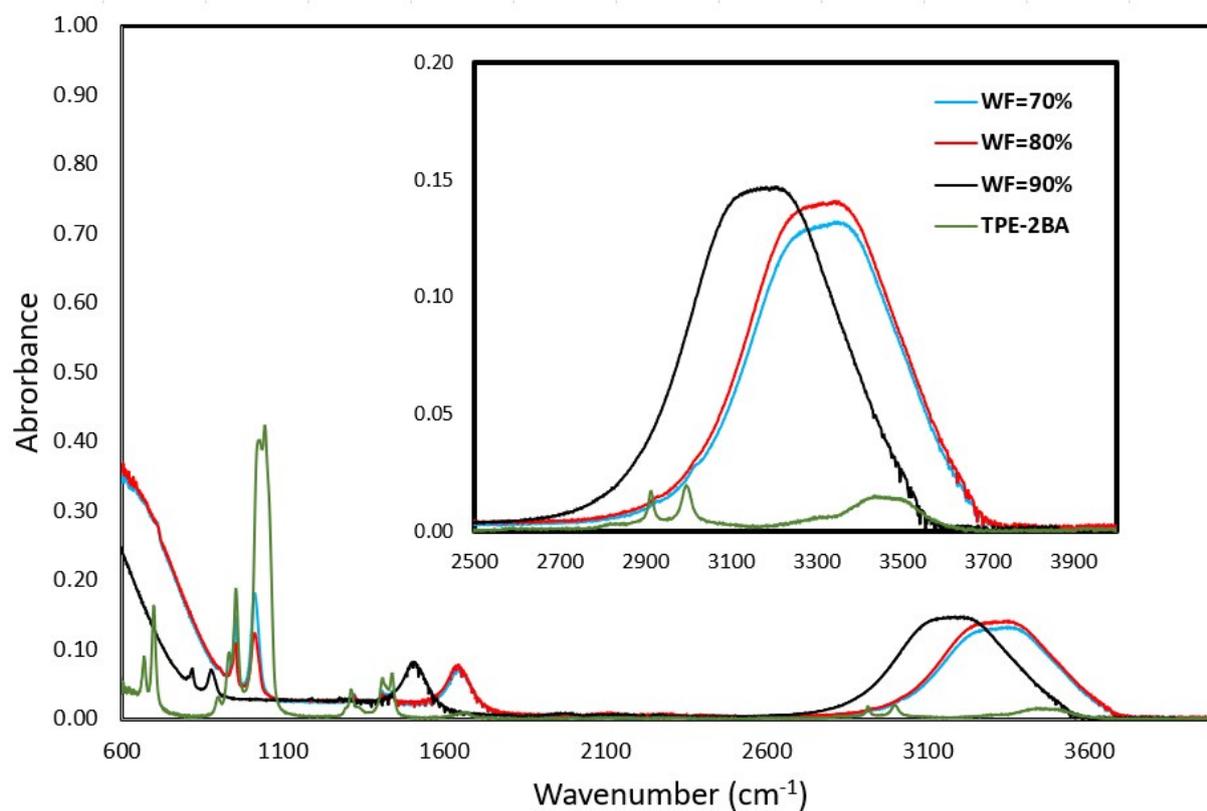
Isothermal titration calorimetry (ITC): ITC was employed (Nano ITC, TA instrument) to compare the binding constant for “TPE-2BA” and “AIE-HBP”. ITC was performed at 4°C where 25 μ l of 50 μ M TPE-2BA solution was injected into 1 mM HBP solution in equal steps of 2.5 μ l. For titration of TPE-2BA molecules 25 μ l of 50 μ M, TPE-2BA solution was injected into DMSO in equal steps of 2.5 μ l.



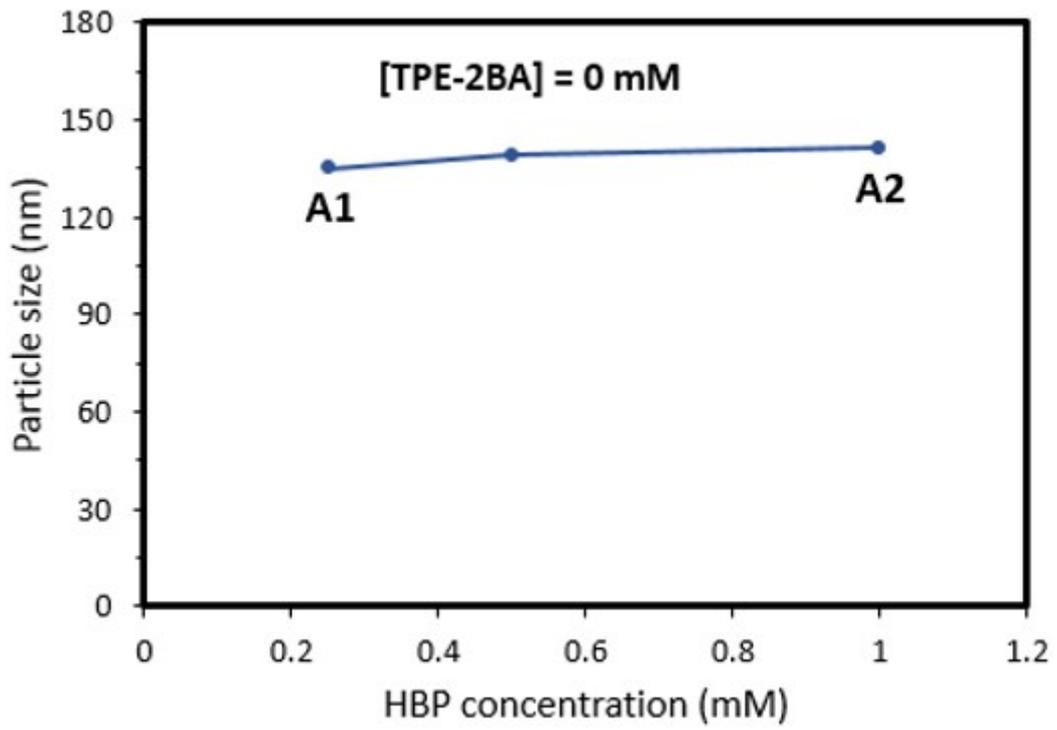
Supplementary S2. Quantum yield measurement for TPE-2BA and AIE-HBP. We found that fluorescence quantum yield of AIE-HBP aggregates depending on the final concentration of HBP with increasing in tracking towards 1 mM. For a constant concentration of HBP, increase in WF significantly enhanced the associated FL quantum yield.



Supplementary S3. Acceptable fluorescence stability was seen for AIE-HBP with 1 mM concentration of HBP, with a negligible decrease over one week at WF= 90%.

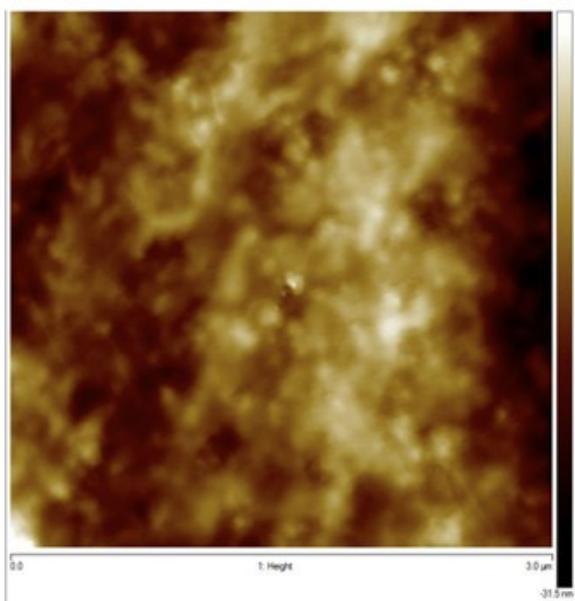


Supplementary S4. Formation of hydrogen bonds between HBP and TPE-2BA. FTIR results revealed that hydrogen bonds significantly formed between TPE-2BA and HBP at different WF= 70, 80, and 90% compared to TPE-2BA alone.

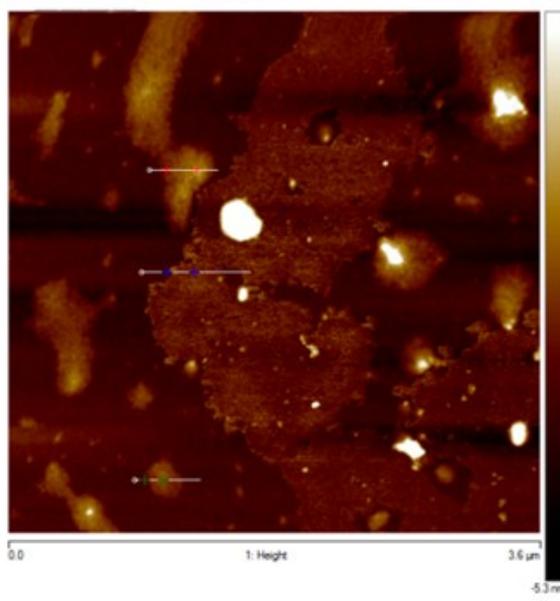


Supplementary S5. HBP particle size at different concentration.

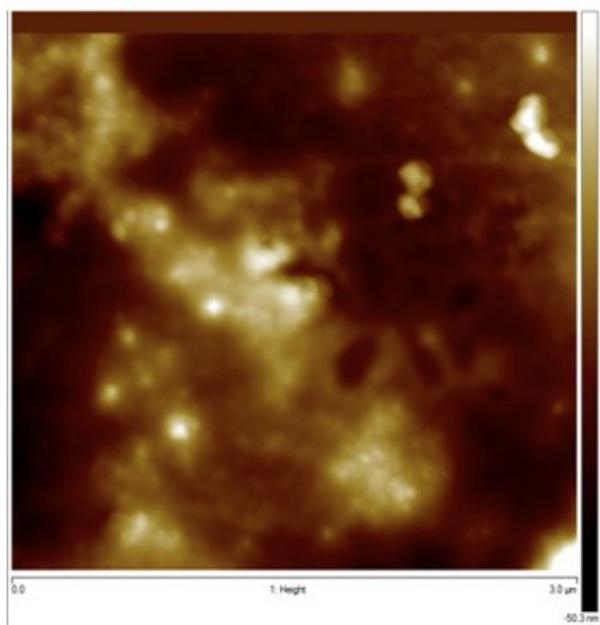
HBP 1mM only.



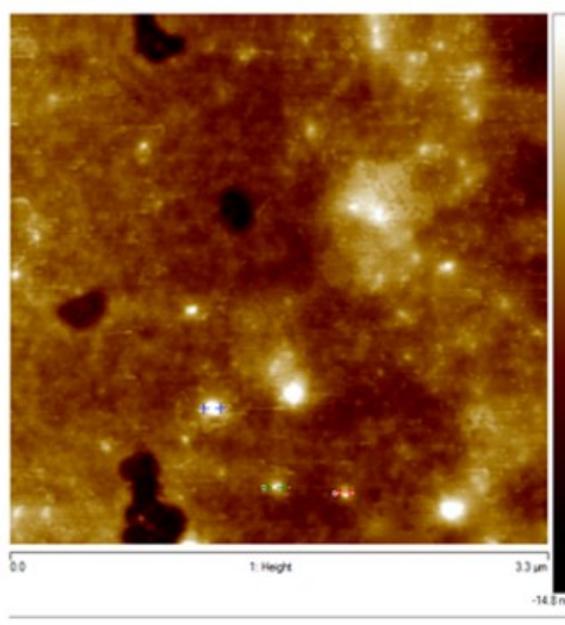
HBP 0.25 mM+ AIE



HBP 0.5 mM+ AIE



HBP 1 mM + AIE



Supplementary S6. AFM images for AIE-HBP at different concentrations of 0, 0.25, 0.0 and 1 mM.

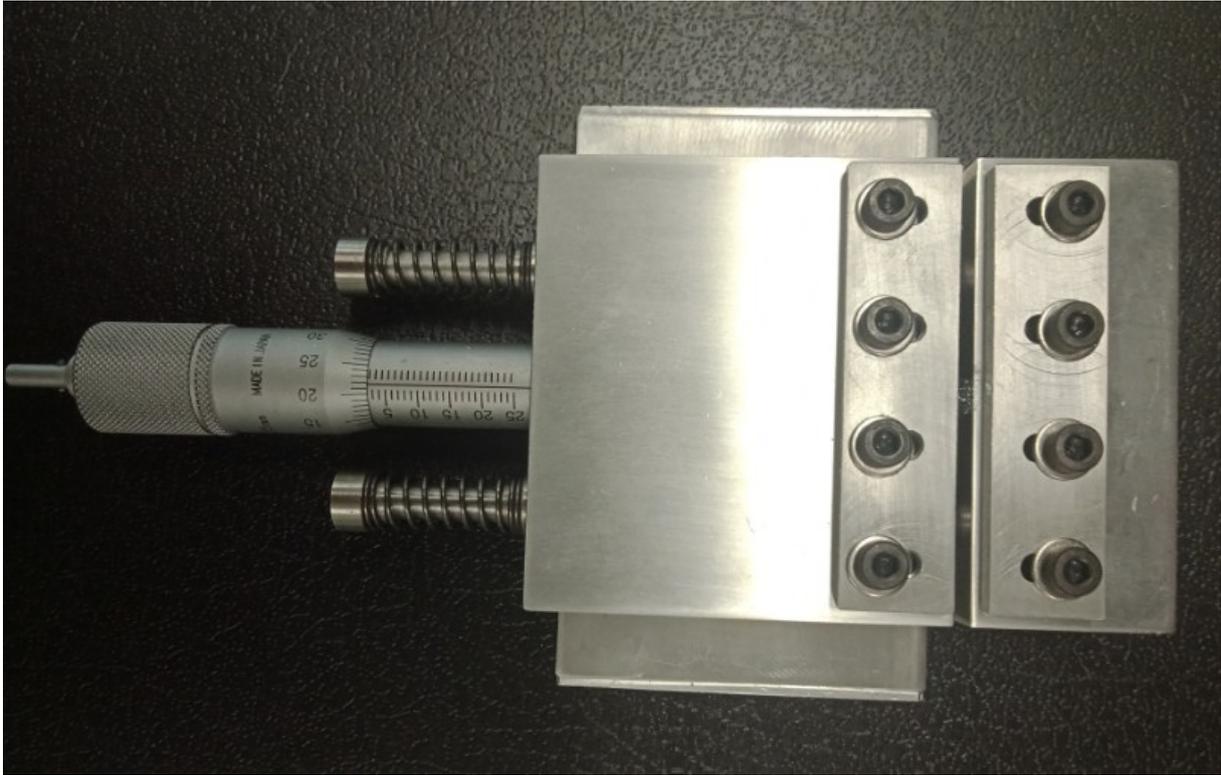


Figure S7. Camera image of highly precise custom-made tension devices.