

## Supporting Information

### Enhanced Liquid Phase Exfoliation of Graphene in Water Using an Insoluble Bis-Pyrene Stabiliser

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## S1. Synthesis and Characterisation of Pyrene-Based Stabilisers

### S1.1. General Information

THF was dried using a PureSolv solvent purification system. All other solvents and reagents used were purchased from commercial suppliers and used without further purification. <sup>1</sup>H-NMR spectra were obtained at room temperature on a Bruker 400 MHz or 500 MHz spectrometer. <sup>13</sup>C-NMR spectra were obtained at 100 or 125 MHz, respectively. All NMR spectra were processed using *MestReNova* NMR software. Chemical shifts are reported in parts per million (ppm) and coupling constants (*J*) reported in Hz. Splitting patterns are reported as follows: singlet (s), doublet (d), triplet (t), quadruplet (q), quintet (quint). Infra-red spectra were recorded as evaporated films or neat using FT/IR spectrometers. Melting points were measured on solids as obtained after chromatography. Mass spectra were obtained using positive or negative electrospray (ESI), atmospheric pressure chemical ionization (APCI) or atmospheric solids analysis probe (ASAP).

### S1.2. Aqueous solubility determination

To a vial charged with **BPS** and fitted with a stirring bar was added D<sub>2</sub>O (0.5 mL) prior to sealing it under air. The resulting suspension was sonicated for ten minutes and then stirred at room temperature for 72 h. The suspension was allowed to settle and the supernatant was filtered through cotton. The concentration of the saturated solution was determined by <sup>1</sup>H-NMR using nitromethane as an internal standard. The solubility of pyrene-based stabilisers **BPS** and **LBPS** in water was below the limit of detection while the solubility of 1-methyl-1-(pyren-1-ylmethyl)pyrrolidinium bromide **MPS** was found to be 11.4 mg/mL.

### S1.3. Synthesis and Characterization

#### S1.3.1 Spectroscopic and Analytical Data

##### *N*-(1-Pyrenylmethyl)pyrrolidine (**3ab**)

To a vial charged with a stirring suspension of 1-bromomethylpyrene<sup>1</sup> (3.50 g, 11.9 mmol) in dry hexane (12.0 mL) at 0 °C was added pyrrolidine (4.0 mL, 47.4 mmol). The stirring mixture was allowed to warm to room temperature and after 21 h the precipitate was filtered under vacuum, dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and washed with saturated aqueous NaHCO<sub>3</sub>. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 50 mL) and the combined organic fractions were dried (MgSO<sub>4</sub>) and concentrated under vacuum. The title product was obtained as an off-white solid (2.83 g, 84%), **mp**: 97 – 100 °C. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.51 (d, *J* = 9.2 Hz, 1 H), 8.24 - 8.12 (m, 4 H), 8.11 - 8.04 (m, 3 H), 8.01 (t, *J* = 7.6 Hz, 1 H), 4.42 (bs, 2 H), 2.73 (bs, 4 H), 1.85 (bs, 4 H); <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>) δ 133.4, 131.3, 130.9, 130.5, 129.5, 127.6, 127.4, 127.2, 126.9, 125.8, 124.9 (2C), 124.9, 124.8, 124.5, 123.9, 58.4, 54.4, 23.6; **IR**  $\nu_{\max}$  (neat/cm<sup>-1</sup>): 2922, 2797, 1456, 1344, 1113, 848; **HRMS** calcd for C<sub>21</sub>H<sub>20</sub>N [M+H]<sup>+</sup>: 286.1590, found 286.1578.

##### 1-(3-(Pyren-1-yl)propyl)pyrrolidine (**3bb**)

To a vial charged with a stirring suspension of 1-(1-pyrenyl)-3-bromopropane<sup>1</sup> (400 mg, 1.24 mmol) in dry hexane (1.20 mL) at 0 °C was added pyrrolidine (413 μL, 4.95 mmol). The mixture was stirred at 50 °C. After 18 h the crude was cooled down to room temperature and dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and washed with saturated aqueous NaHCO<sub>3</sub>. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 50 mL) and the combined organic fractions were dried (MgSO<sub>4</sub>) and concentrated under vacuum. The title product was obtained as an orange oil (389 mg, >99%), <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 8.31 (d, *J* = 9.2 Hz, 1H), 8.16 (dd, *J* = 7.7, 4.6 Hz, 2H), 8.10 (t, *J* = 8.0 Hz, 2H), 8.04 - 7.97 (m, 3H), 7.89 (d, *J* = 7.6 Hz, 1H), 3.40 (t, *J* = 7.8 Hz, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.53 (bs, 4H), 2.10 (quint, *J* = 7.8 Hz, 2H), 1.80 (bs, 4H); <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>) δ 136.8, 131.6, 131.1, 129.9, 128.8, 127.6, 127.3, 127.3, 126.7, 125.9, 125.2, 125.1, 124.9 (2C), 124.8, 123.6, 56.4, 54.4, 31.6, 31.3, 23.6; **IR**  $\nu_{\max}$  (neat/cm<sup>-1</sup>): 2937, 904, 846, 723; **HRMS** calcd for C<sub>23</sub>H<sub>24</sub>N [M+H]<sup>+</sup>: 314.1908, found 314.1889.

##### 1-Methyl-1-(pyren-1-ylmethyl)pyrrolidinium bromide (MPS)

A solution of 1-bromomethylpyrene<sup>2</sup> **1a** (148 mg, 0.5 mmol) and *N*-methylpyrrolidine **2a** (53 μL, 0.5 mmol) in THF (1.3 mL) was stirred in a vial sealed under air at 60 °C. After 18 h the mixture was allowed to cool to room temperature and the precipitate was filtered under vacuum, washed with THF and then Et<sub>2</sub>O. The title product was obtained as a white solid (190 mg, >99%), **mp**: decomposes above 200 °C. <sup>1</sup>H-NMR (500 MHz, MeOD-d<sub>4</sub>) δ 8.58 (d, *J* = 9.2 Hz, 1H), 8.34 - 8.31 (m, 4H), 8.24 (d, *J* = 8.5 Hz, 2H), 8.16 (d, *J* = 8.8 Hz, 1H), 8.12 (t, *J* = 7.6 Hz, 1H), 5.40 (s, 2H), 3.86 - 3.81 (m, 2H), 3.62 - 3.58 (m, 2H), 3.07 (s, 3H), 2.31 - 2.25 (m, 4H); <sup>13</sup>C-NMR (126 MHz, MeOD-d<sub>4</sub>) δ 134.6, 133.0, 132.6, 132.5, 131.7, 130.7, 130.3, 128.2, 127.8, 127.6, 127.3, 126.1, 126.0, 125.4, 123.5, 122.5, 68.8, 64.4, 26.5, 22.0; **IR**  $\nu_{\max}$

(neat/cm<sup>-1</sup>): 2972, 1587, 1460, 1404, 1240, 1177, 1058, 919; **HRMS** calcd for C<sub>22</sub>H<sub>22</sub>N [M]<sup>+</sup>: 300.1746, found 300.1733.

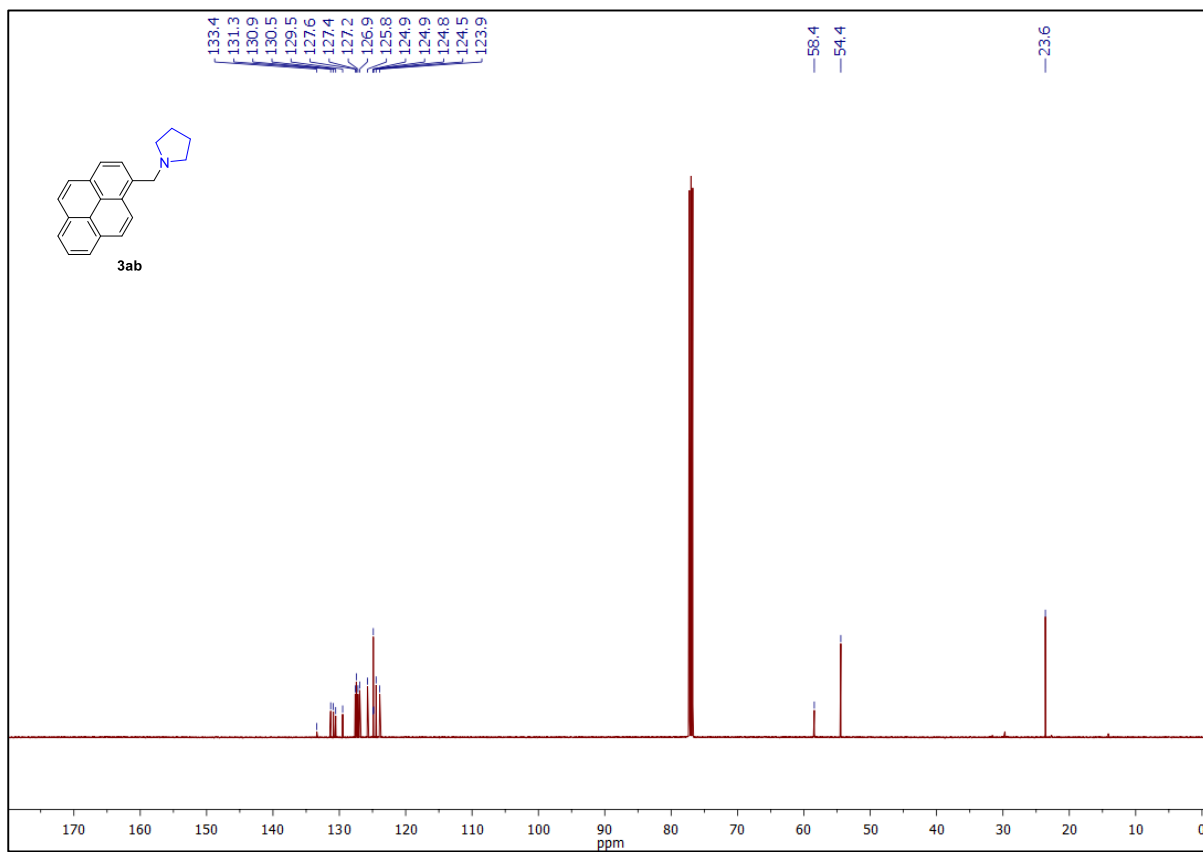
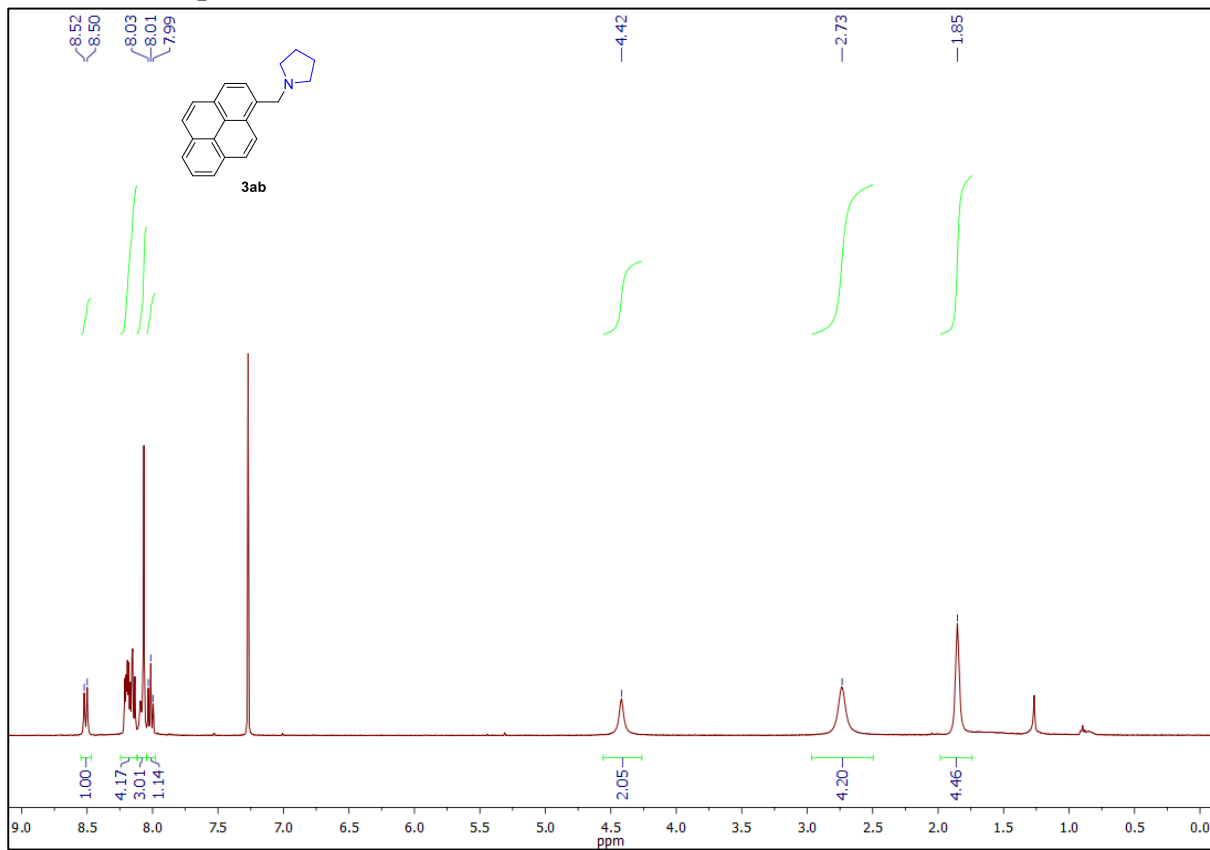
### ***N,N*-Di(1-pyrenylmethyl)pyrrolidinium bromide (pyrene tweezer-1) (BPS)**

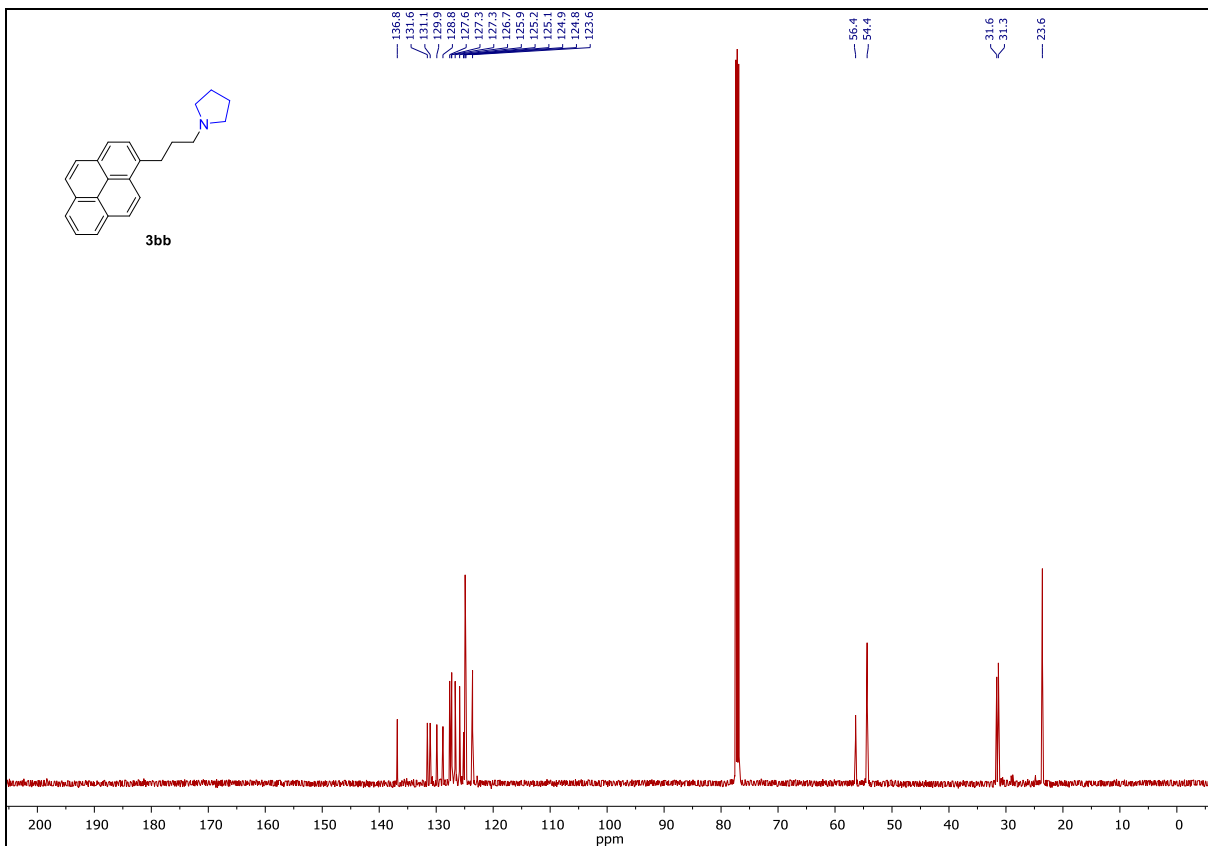
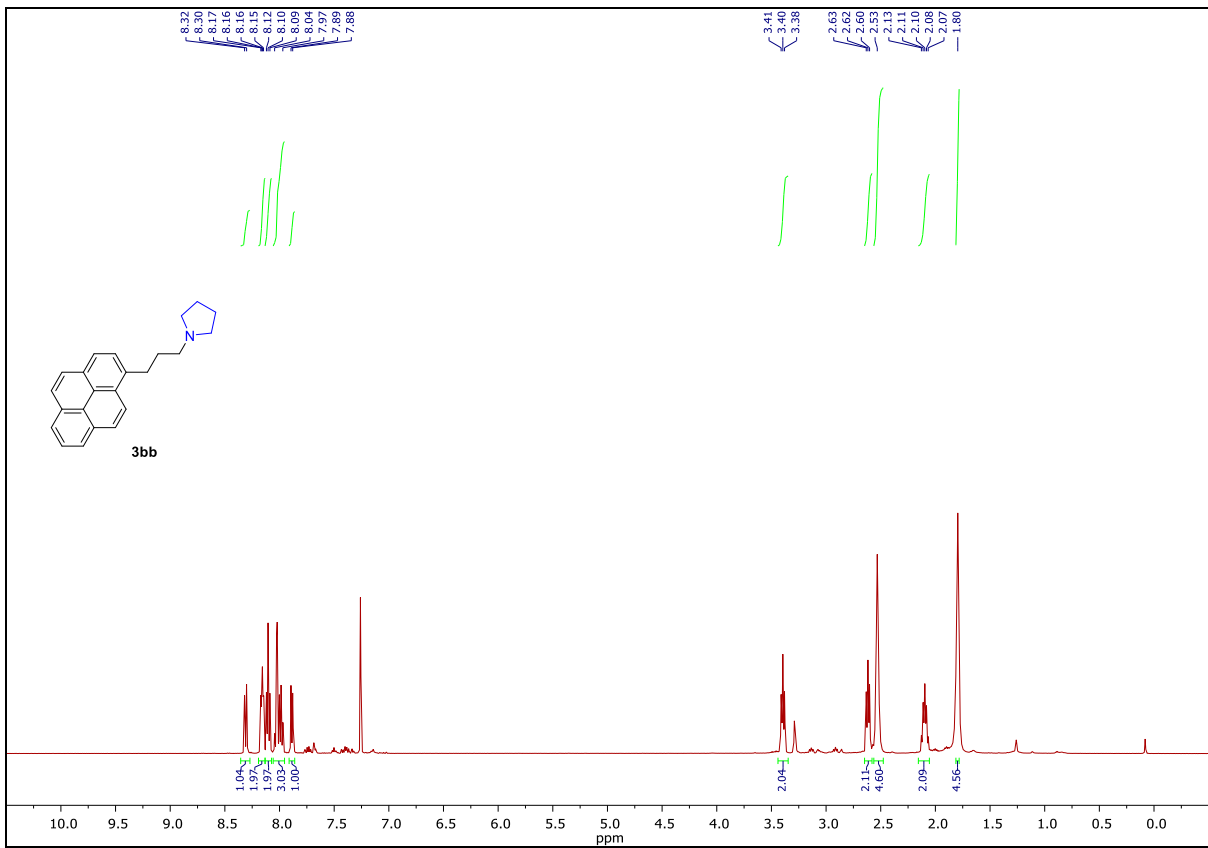
A solution of 1-bromomethylpyrene<sup>1</sup> (432 mg, 1.46 mmol) and 1-(pyren-1-ylmethyl)pyrrolidine **3ab** (418 mg, 1.46 mmol) in THF (4.3 mL) was stirred in a vial sealed under air at 60 °C. After 18 h the mixture was allowed to cool to room temperature and the precipitate was filtered under vacuum, washed with THF and then Et<sub>2</sub>O. The title product was obtained as an off-white solid (759 mg, 90%), **mp**: decomposes above 165 °C. **<sup>1</sup>H-NMR** (500 MHz, MeOD-d<sub>4</sub>) δ 8.37 - 8.33 (m, 6 H), 8.31 - 8.14 (m, 10 H), 8.10 (t, *J* = 7.8 Hz, 2 H), 5.55 (s, 4 H), 3.79 (bs, 4 H), 2.17 (bs, 4 H); **<sup>13</sup>C-NMR** (125 MHz, MeOD-d<sub>4</sub>) δ 134.8, 133.5, 133.2, 132.6, 131.6, 131.0, 130.5, 128.2, 127.9, 127.8, 127.4, 126.2, 126.1, 125.4, 123.0, 121.7, 61.7, 59.6, 21.9; **IR** ν<sub>max</sub> (neat/cm<sup>-1</sup>): 2964, 1462, 1351, 1235, 1186, 1064, 853; **HRMS** calcd for C<sub>38</sub>H<sub>30</sub>N [M]<sup>+</sup>: 500.2373, found 500.2357.

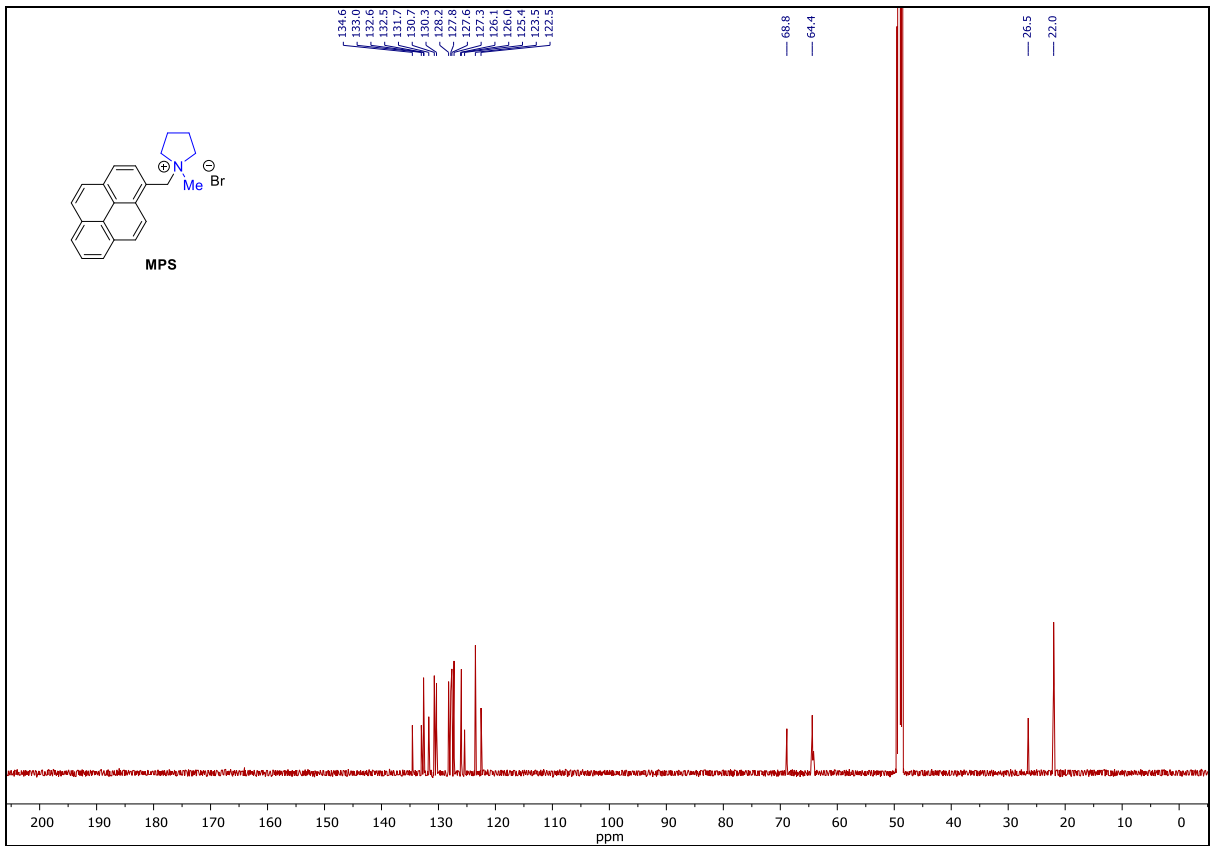
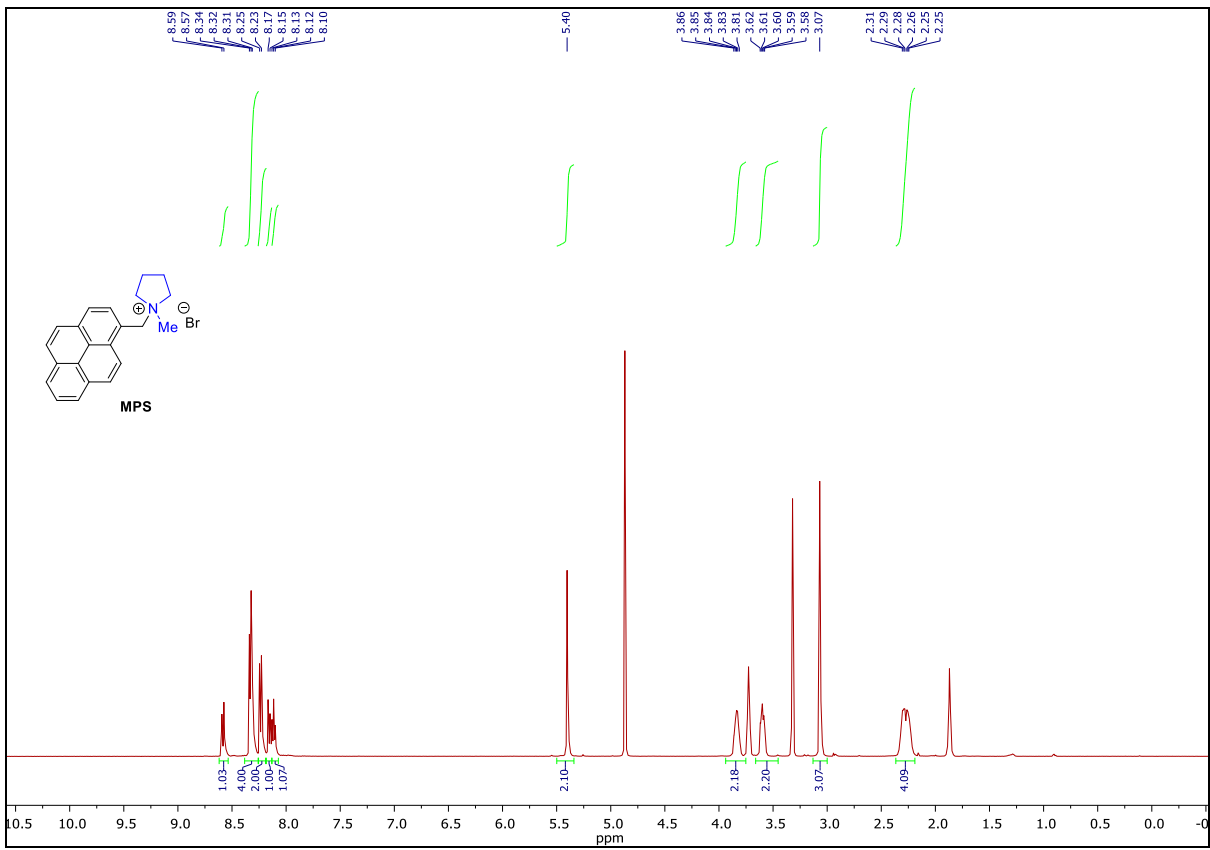
### **1,1-Bis(3-(pyren-2-yl)propyl)pyrrolidin-1-ium bromide (pyrene tweezer-2) (LBPS)**

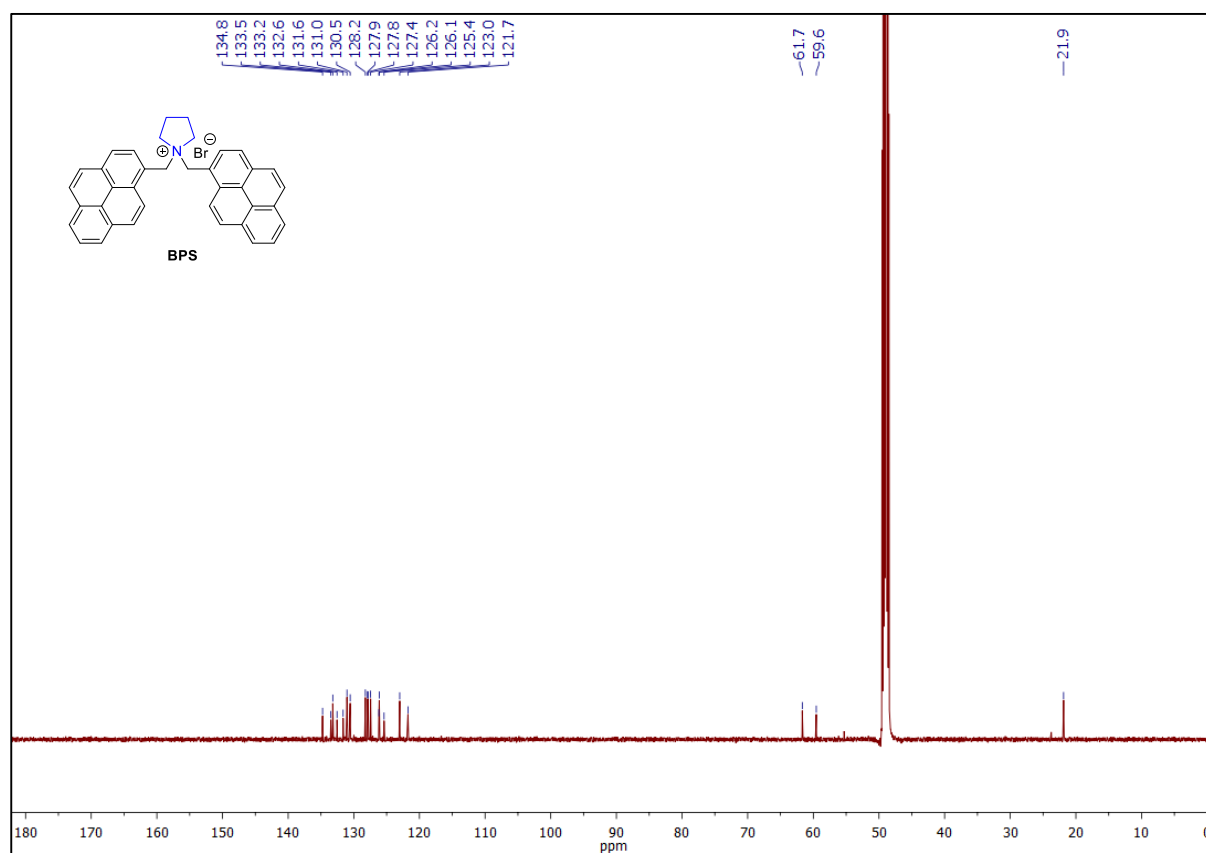
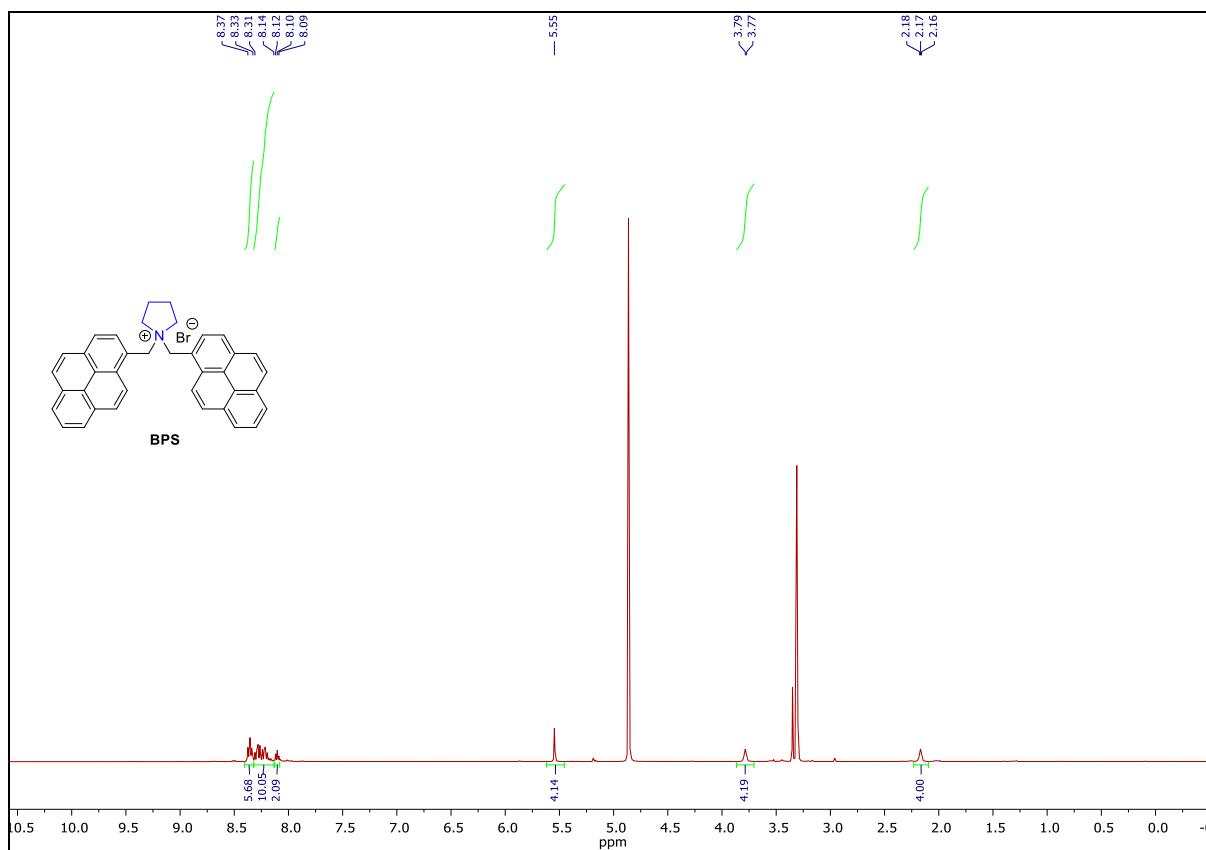
A solution of 1-(1-pyrenyl)-3-bromopropane<sup>2</sup> (368 mg, 1.14 mmol) and 1-(3-(pyren-1-yl)propyl)pyrrolidine **3bb** (382 mg, 1.22 mmol) in THF (3.4 mL) was stirred in a vial sealed under air at 60 °C. After 18 h the mixture was allowed to cool to room temperature and the precipitate was filtered under vacuum, washed with THF and then Et<sub>2</sub>O. The title product was obtained as an off-white solid (198 mg, 27%), **mp**: 235 °C. **<sup>1</sup>H-NMR** (500 MHz, MeOD-d<sub>4</sub>) δ 8.17 - 8.14 (m, 4H), 8.09 (d, *J* = 7.7 Hz, 2H), 8.00 - 7.94 (m, 6H), 7.89 (d, *J* = 8.9 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 2H), 3.50 (t, *J* = 7.2 Hz, 4H), 3.39 - 3.34 (m, 4H), 3.24 (t, *J* = 7.4 Hz, 4H), 2.15 (bs, 4H), 2.04 - 1.96 (m, 4H); **<sup>13</sup>C-NMR** (125 MHz, DMSO-d<sub>6</sub>) δ 134.8, 130.9, 130.3, 129.5, 128.1, 127.5, 127.4, 127.3, 126.7, 126.2, 125.1, 124.9, 124.9, 124.2, 124.1, 123.2, 62.54, 58.4, 29.0, 25.0, 21.5; **IR** ν<sub>max</sub> (neat/cm<sup>-1</sup>): 3419, 3044, 2941, 1602, 1586, 1461, 1184, 1085 862; **HRMS** calcd for C<sub>42</sub>H<sub>38</sub>N [M]<sup>+</sup>: 556.2998, found 556.2981.

### S1.3.2 NMR Spectra

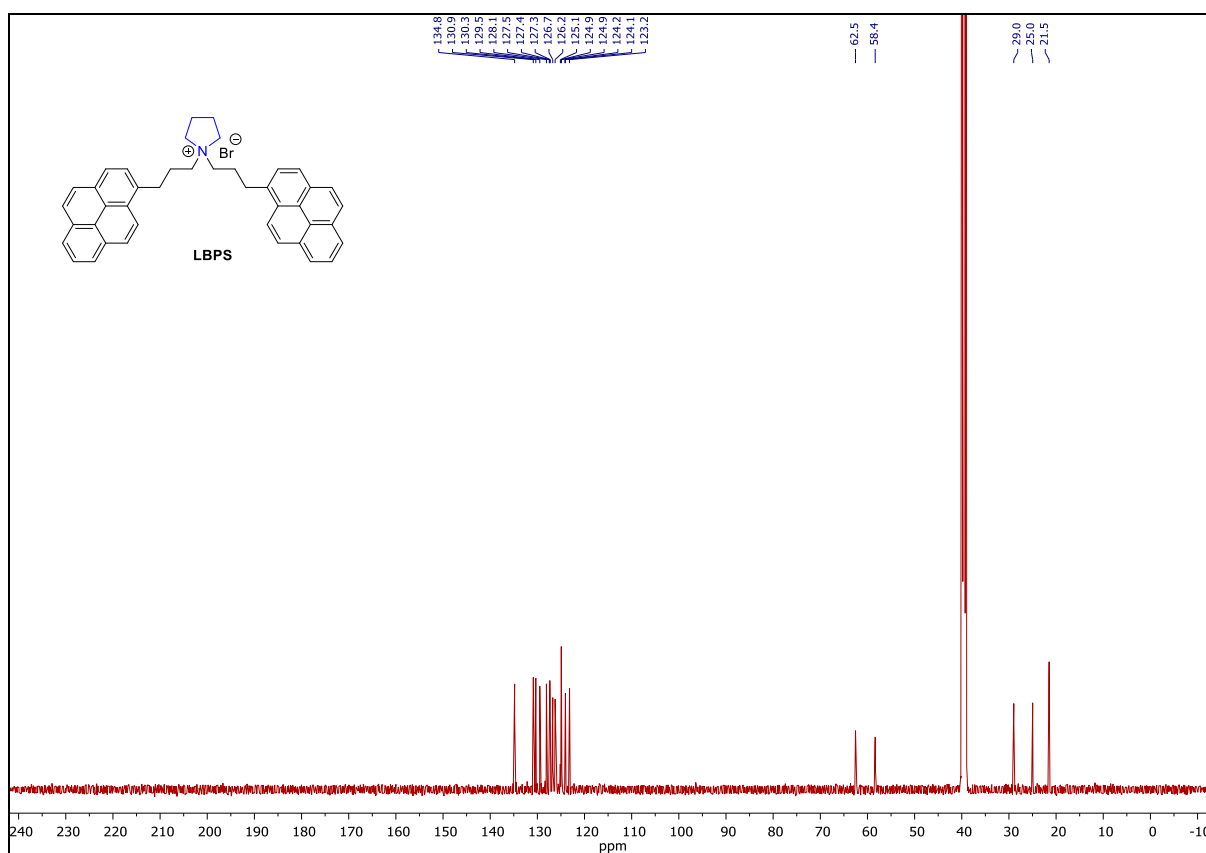
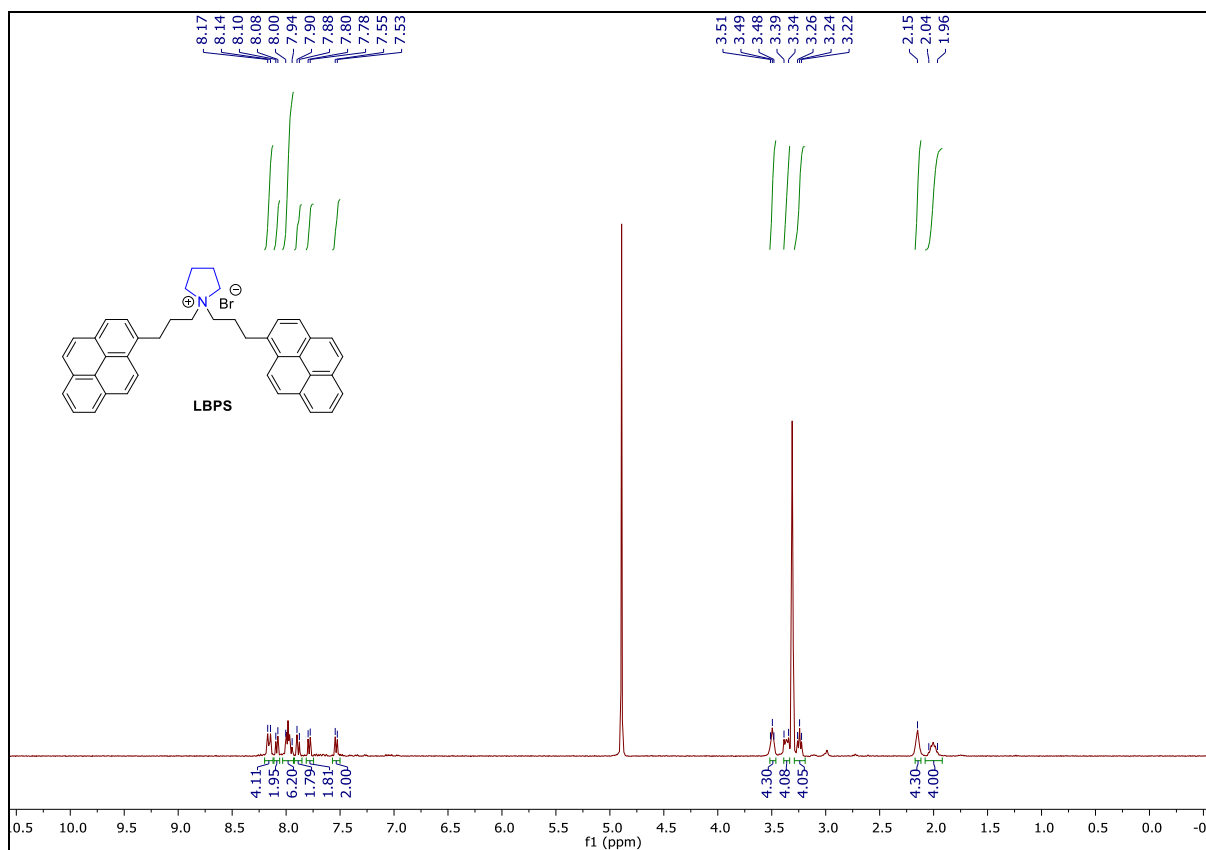




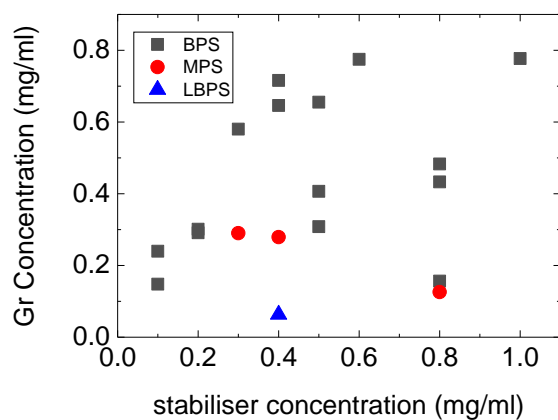






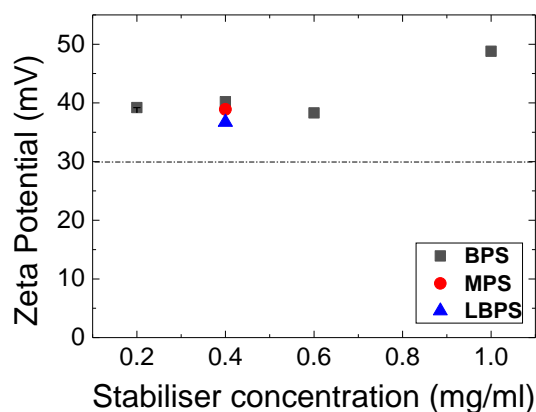


## S2. Characterisation of Graphene Dispersions



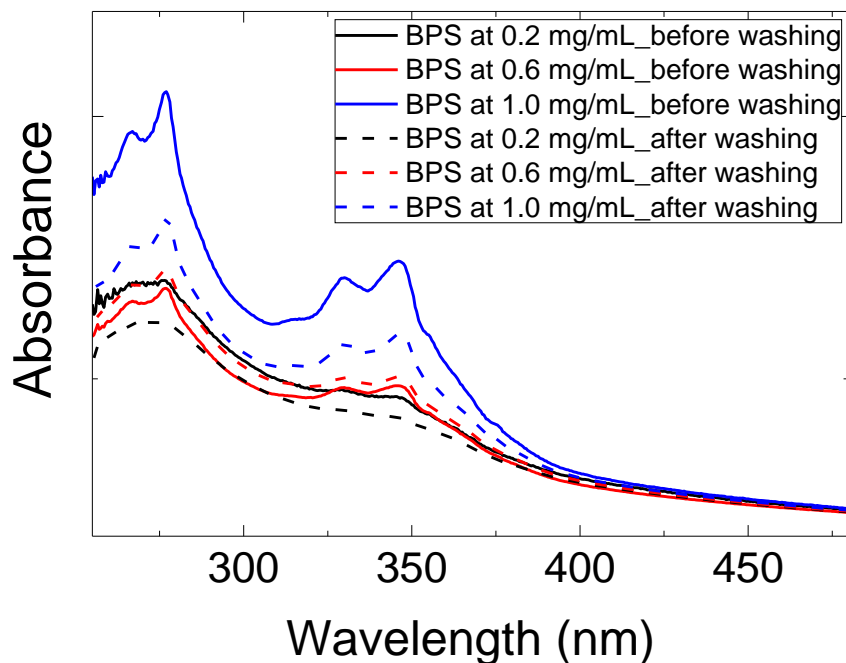
**Figure S1** Graphene concentrations obtained for different graphene dispersions.

Due to the nature of bath sonication, there is batch to batch variance of exfoliation efficiency observed for LPE graphene dispersions. However, despite the varying final concentration of graphene dispersions prepared, there is a trend of increasing final graphene dispersion concentration observed with increasing initial BPS concentration.



**Figure S2** Zeta Potential measured for the graphene dispersions. A guidance line at 30 mV was added to show stability of the dispersions.

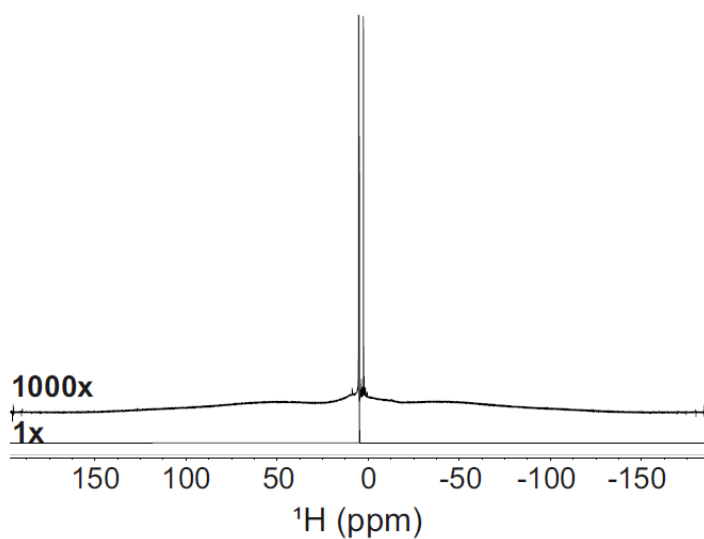
The colloidal stability of the produced graphene dispersions was studied by measuring zeta potential. All the graphene dispersions prepared with the pyrene stabilisers in this study shows zeta potential values higher than 30 mV, demonstrating their excellent colloidal stability.



**Figure S3** UV-vis spectra of graphene dispersions prepared with BPS stabilisers at different concentrations, before and after washing step.

Because of the insolubility of the BPS molecules in water, washing step using centrifugation, exchanging supernatant solution with DI water does not change the concentration of pyrene present in the final graphene solution even after the washing step. In case of MPS, which is soluble in water, the pyrene peaks observed below 400 nm are significantly reduced after the washing step.

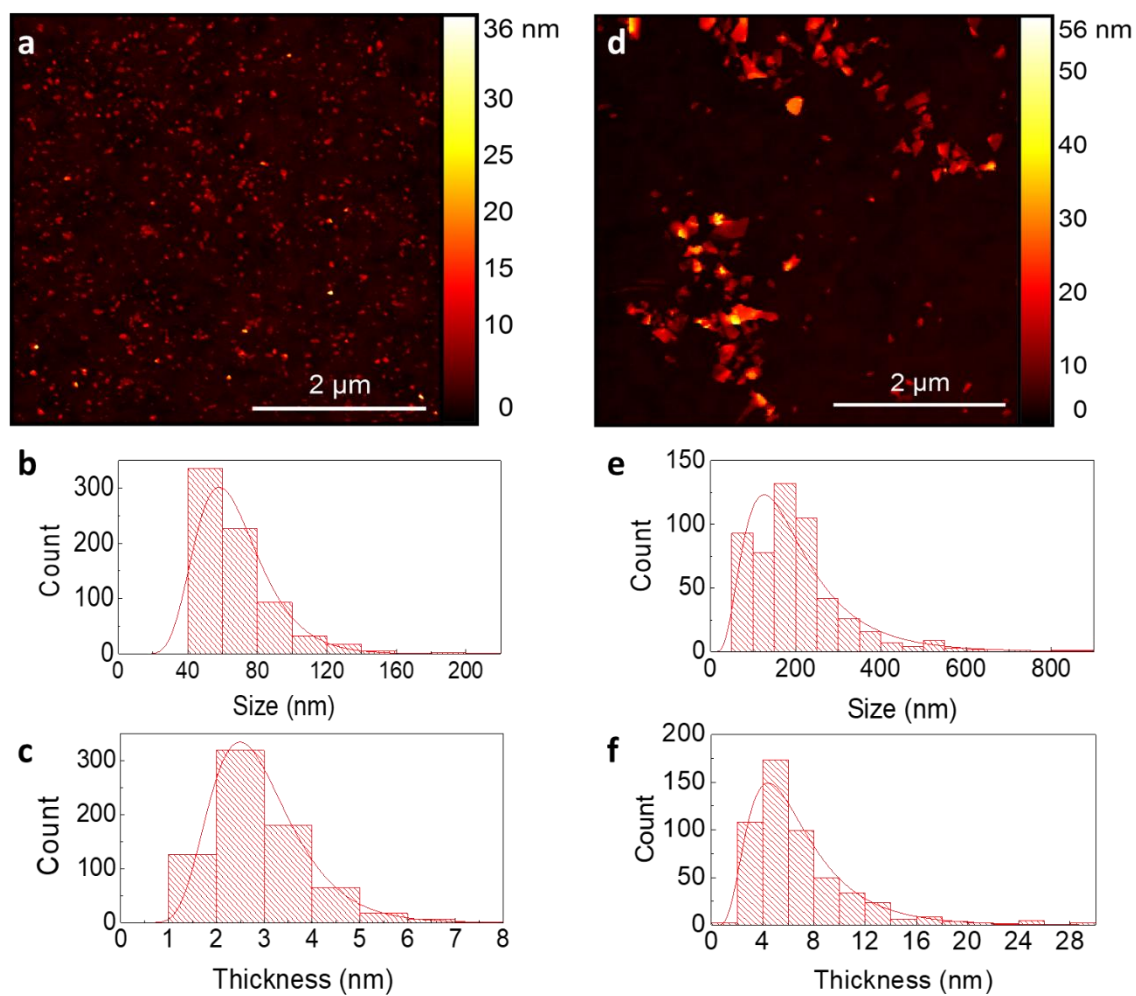
### S3. Wide $^1\text{H}$ spectrum



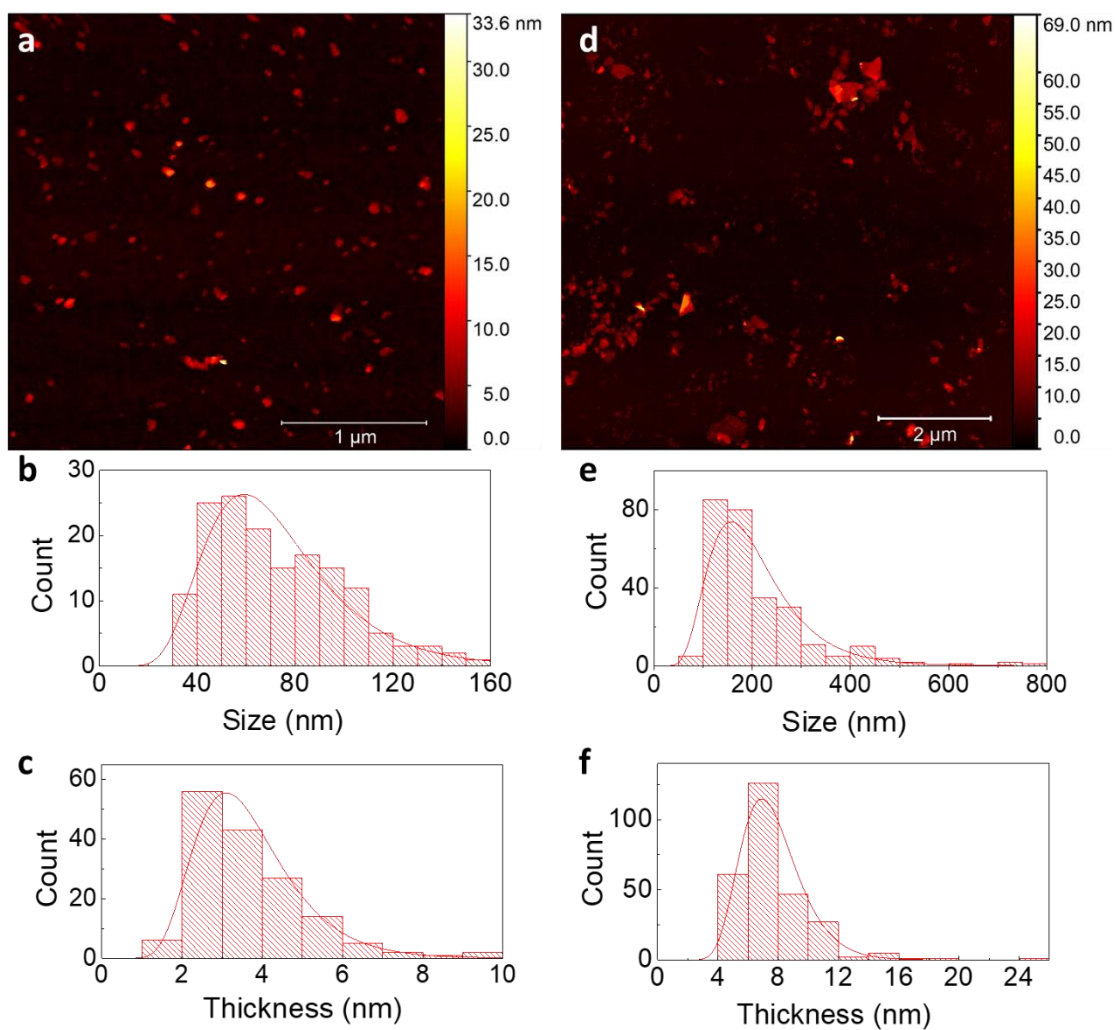
**Figure S4** Wide  $^1\text{H}$  spectrum of a graphene dispersion, of concentration 0.8 mg/mL, with BPS at 0.6 mg/mL in  $\text{D}_2\text{O}$  at 1x and 1000x zoom.

This wide  $^1\text{H}$  spectrum was acquired in 4.3 h using  $19^\circ$  pulses, a spectral width of 192.3 kHz, 256000 complex data points, and a recycle time of 0.77 s. It confirms that most of the proton signal intensity seen in the standard  $^1\text{H}$  and DOSY spectra (main text, **Figure 1(c)** and **(d)**, respectively) comes from very broad signals.

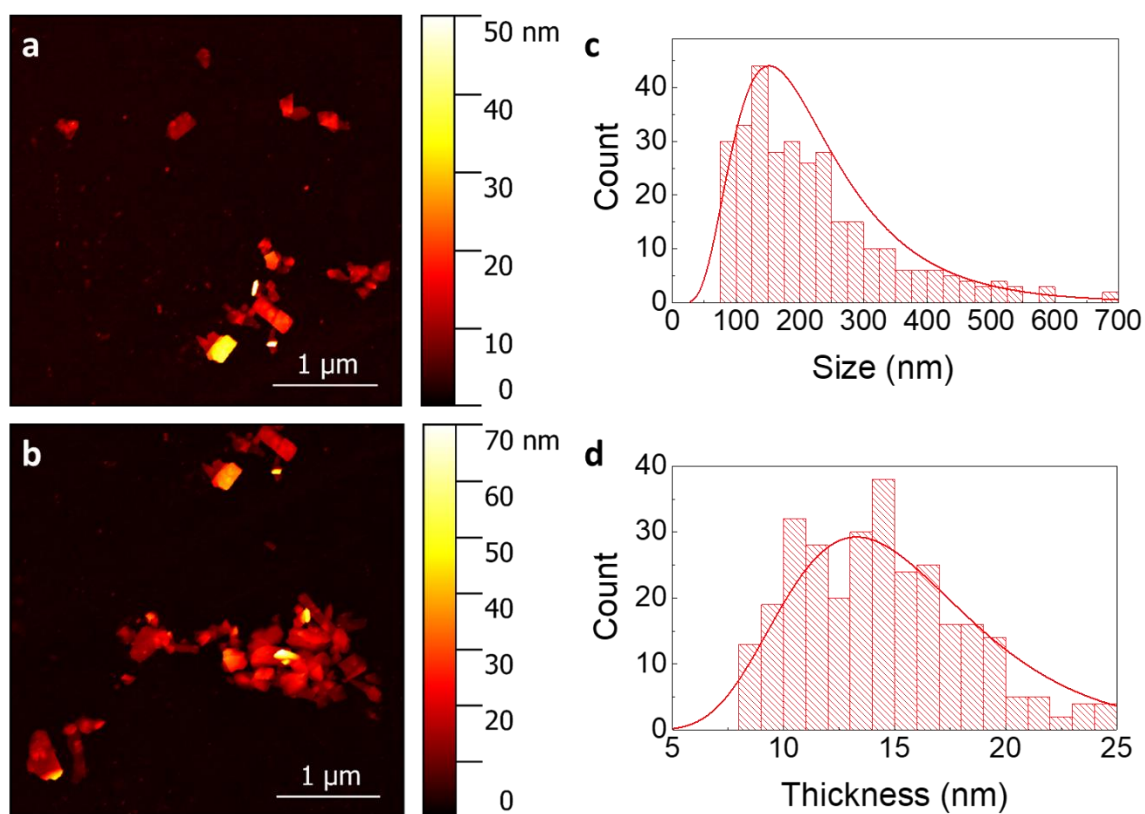
## S4. AFM Analysis



**Figure S5** AFM analysis of graphene nanosheets for sample with BPS at 0.4 mg/mL. **(a)** AFM image, **(b)** lateral size and **(c)** thickness distribution for supernatant and **(d)** AFM image, **(e)** lateral size and **(f)** thickness distribution for the dispersion.



**Figure S6** AFM analysis of graphene nanosheets for sample with BPS at 0.6 mg/mL. **(a)** AFM image, **(b)** lateral size and **(c)** thickness distribution for supernatant and **(d)** AFM image, **(e)** lateral size and **(f)** thickness distribution for the dispersion.



**Figure S7** AFM analysis of graphene nanosheets for sample with MPS at 0.4 mg/mL. **(a-b)** AFM images, **(c)** lateral size and **(d)** thickness distribution for the dispersion.

AFM is one of the most popular method for characterisation of the lateral size and thickness distribution of the exfoliated graphene nanosheets. For statistical analysis, AFM images of large area (typically between 25 and 100  $\mu\text{m}^2$  size) with more than two hundreds of individual flakes were used, or in some cases, several images were used together. Only individual flakes were counted towards statistics and aggregated nanosheets were excluded. The AFM sample is prepared by drop casting dilute (conc. =  $\sim 5 \mu\text{g/mL}$ ) graphene dispersion on clean silicon wafer. The distribution histograms for each samples are shown together in each figures (**Figure S4 – S6**).

## References

1. Nishimura, T. *et al.* A simple visual sensor with the potential for determining the concentration of fluoride in water at environmentally significant levels. *Chem. Commun.* **49**, 478–480 (2013).
2. Moon, S. J., Park, S. H., Jaworski, J. & Jung, J. H. Pyrene-imidazolium complexed graphene for the selective fluorescent detection of G-quadruplex forming DNA. *Chem. Commun.* **49**, 11698–11700 (2013).