# SUPPORTING INFORMATIONS

**Nanoscale insight into the exfoliation mechanism of graphene with organic dyes: effect of charge, dipole and molecular structure**

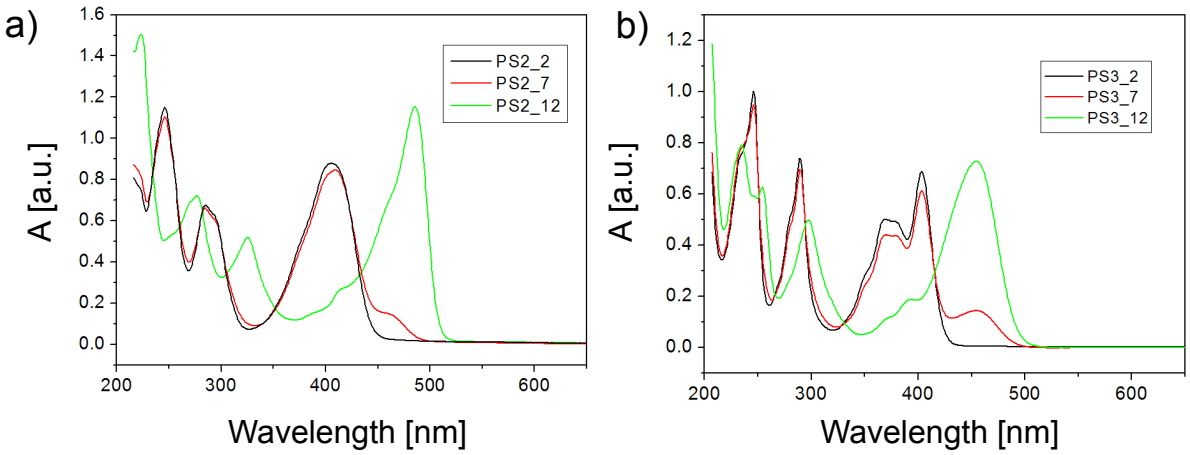



Fig. S1: Absorption spectra of a) PS2, and b) PS3 dyes at different pH.

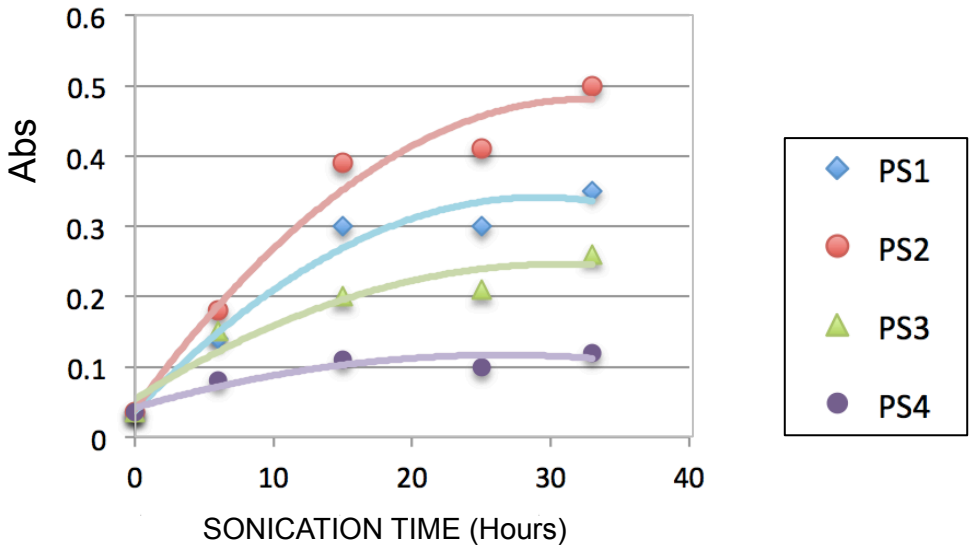
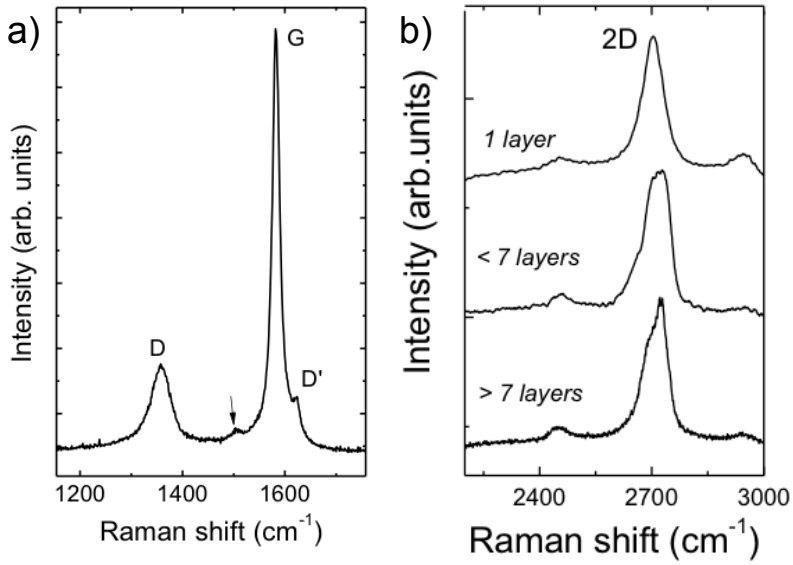



Fig. S2: Estimation of dissolved material by measuring optical absorption of the different solutions at 650 nm for different sonication times. The lines are a reference for the eye.




c)

| Molecule | % single layers | % thin sheets (2-7 layers ) | % thick sheets (>7 layers) | Total |
|---|---|---|---|---|
| PS1 | 18 | 68 | 14 | 100 |
| PS2 | 15 | 55 | 31 | 100 |
| PS3 | 22 | 65 | 13 | 100 |
| PS4 | 9 | 55 | 36 | 100 |

Fig. S3. Raman analysis of graphene-pyrene composites, obtained by spin coating the sonicated solutions on silicon. a) typical first order peaks, the peak at 1505 $cm^{-1}$ (black arrow) is related to the molecules residual. b) Typical shapes of 2D peaks obtained for monolayers, thin sheets, less than 7 layers and thick flakes. c) Raman statistical analysis of sheet thickness. Suspensions drop cast on $SiO_2$, statistic on 60 to 70 flakes for each dye.

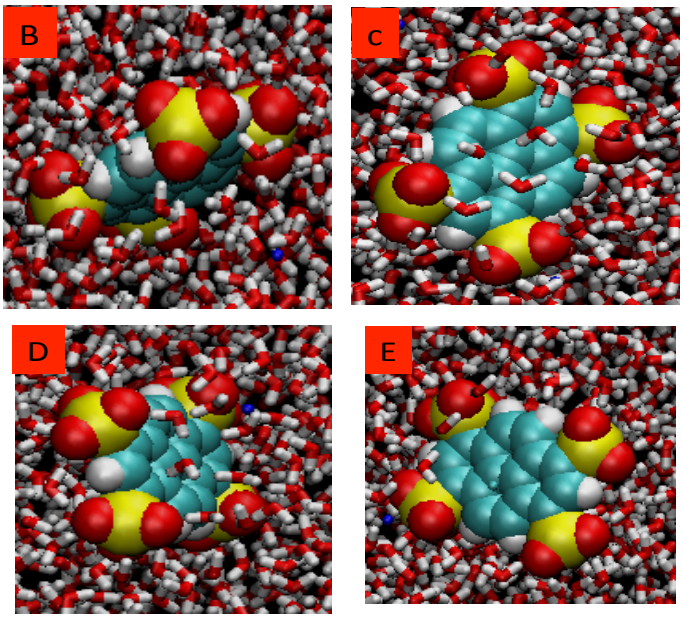



Fig. Snapshots PS4 molecules at different distances from graphene, as seen from below the graphene layer. The letters correspond to selected points in the PMF curve shown in fig. 8b in main text.

Table S1. The interaction energies (kcal/mol) of the component functional groups (pyrene core, $SO_3$, OH) of adsorbed PSx molecules with graphene.

| | graph-pyrene | graph-$SO_3$ | graph-OH | Total | graph-$SO_3$ normalized | graph-OH normalized |
|---|---|---|---|---|---|---|
| PS1 | -22.93 ± 0.09 | -4.94 ± 0.04 | - | -27.87 | -4.94 | - |
| PS2 | -21.75 ± 0.06 | -9.63 ± 0.06 | -3.22 ± 0.02 | -34.60 | -4.82 | -1.61 |
| PS3 | -21.63 ± 0.09 | -14.91 ± 0.19 | -1.63 ± 0.05 | -38.19 | -4.97 | -1.64 |
| PS4 | -21.59 ± 0.05 | -19.99 ± 0.08 | - | -41.59 | -4.99 | - |

* The term “normalized” refers to the interaction energy between graphene and all the functional groups of a given type (graph-pyrene, graph-SO3, or graph-OH) divided by the number of the functional groups of that type within the molecule.
* “Total” refers to the interaction energy between graphene and the whole molecule.

Table S2. The interaction energies (kcal/mol) of the component functional groups (pyrene core, SO3, OH) of adsorbed PSx molecules with surrounding aqueous medium.

| | solv-pyrene | | | solv-$SO_3$ | solv-OH | Total | solv-SO3 normalized | solv-OH normalized |
|---|---|---|---|---|---|---|---|---|
| | Van der Waals | Electrostatic | Total | | | | | |
| PS1 | -13.22 ± 0.02 | -4.83 ± 0.03 | -18.05 | -69.01 ± 0.36 | - | -87.06 | -69.01 | - |
| PS2 | -11.98 ± 0.05 | -2.40 ± 0.17 | -14.38 | -138.82 ± 0.71 | -21.75 ± 0.31 | -174.95 | -69.41 | -10.87 |
| PS3 | -11.65 ± 0.04 | -4.25 ± 0.11 | -15.90 | -205.29 ± 3.7 | -11.46 ± 0.24 | -232.66 | -68.43 | -11.46 |
| PS4 | -11.37 ± 0.03 | -8.91 ± 0.20 | -20.28 | -259.07 ± 7.61 | - | -279.35 | -64.77 | - |

* The term “normalized” refers to the interaction energy between the aqueous medium and all the functional groups of a given type (solv-pyrene, solv-SO3, or solv-OH) divided by the number of the functional groups of that type within the molecule.
* “Total” refers to the interaction energy between the aqueous medium and the whole molecule.

Table S3. Hydration free energies of PSx ions.

| | Hydration energy (kcal/mol) |
|---|---|
| PS1 | -91.96 |
| PS2 | -299.77 |
| PS3 | -379.24 |
| PS4 | -574.26 |