**Flexible Film Materials from Conjugated Dye-Modified Polymer Surfactant-Induced Aqueous Graphene Dispersions.**

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PVAPery composition

The number of perylene units by polymer chains in PVAPery was calculated as follows:

We assume that the product is a copolymer formed by units of vinyl alcohol (VA, denoted by y) and PDI-modified VA (PDI_VA, denoted by x) (scheme 1).
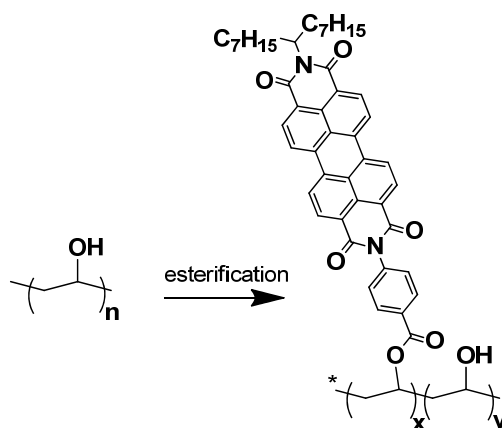
Scheme 1

Considering that the average molecular weight of PVA is 90000 g.mol^{-1} and the molar mass of VA is 44 g.mol^{-1}, the number of units of VA in PVA before reaction with perylene is **$n = 2045$**

If we assume that under the conditions of esterification the initial number of VA units is maintained:

$$n = x + y = 2045 \qquad \text{Eq. (1)}$$

As we used a PVA with 15 wt. % of perylene the number of PDI_VA and VA units can be calculated using the following equation:

$$\frac{y.M_{PDI\_VA}}{x.M_{VA}+y.M_{PDI\_VA}} * 100 = 15 \quad \text{Eq.(2)}$$

where MPDI_VA is 794 g.mol^{-1}.

Thus, from equation 2 the number of PDI_VA units per polymer chain is 19,8.

Raman spectroscopy

Raman spectroscopy can be used both to estimate the number of layers and to assess the quality of graphene samples.[1,2,3] The Raman spectra of graphite and single layer graphene obtained with 514.5 nm laser excitation are given in Figure S1, along with the corresponding band assignments.
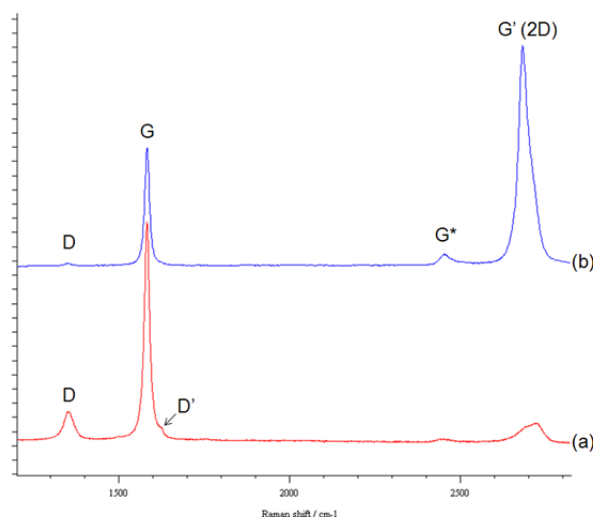

Fig. S1 Raman spectra of (a) slightly defected graphite and (b) single layer graphene.

The most important features in the Raman spectra of graphene are the G band appearing at around 1580 cm^{-1}, the second order 2D (or G') band at around 2700 cm^{-1} and the disorder-induced D and D´ bands at 1350 cm^{-1} and 1620 cm^{-1}, respectively.[1,2] A slightly defected graphite sample was used to highlight the disorder modes. The G band is a doubly degenerate phonon mode at the Brillouin-zone (BZ) center (Γ point) which is Raman active for sp^2 carbon networks. The D and its second order 2D bands both originate from a double resonance process, reflecting the characteristics of phonon dispersions and electronic band structures around the corner (K point) in the BZ. Finally, the D´ band can be assigned to an intra-valley double resonance process involving electronic states around the K point.[4]

Some examples of Raman spectra obtained from several graphene flakes, in the Raman shift region between 1200 – 3200 cm^{-1}, are presented in Figure S2. All spectra are shown with the same abscissa scale. A very high level of background fluorescence generates some difficulties in the analysis of many of the spectra, however, the presence of some of the resonant perylene modes can be clearly seen. A variety of layer thicknesses were observed, and as an example a bilayer graphene sample is identified in the Figure.

The appearance of RRS modes due to perylene[5,6] in the PVAPery polymer occur since the vibrational bands are in resonance with the electronic transitions of the dye molecules. Whilst the Raman spectrum of perylene in powder form was completely impossible to obtain at a laser excitation wavelength of 514.5 nm due to the very high fluorescence generated, which could not be quenched to an acceptable level using conventional laser bleaching methods, in the PVAPery/Gr system on the Si/SiO$_2$ substrate the bands could be clearly observed. This suggests that the PVAPery/Gr system provides a route for quenching the fluorescence, probably through the

interaction with graphene, as was demonstrated very recently by Kozhemyakina et al.[7].

It should be pointed out that no RRS bands were observed when a 785 laser was employed.
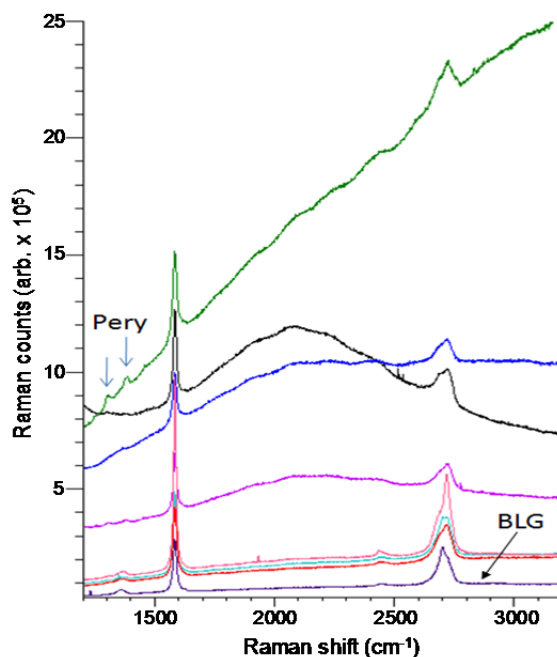

Figure S2. Raman spectra recorded from different graphene flakes.

Raman map analysis

Raman maps were measured using Renishaw Streamline imaging, employing a 100x objective lens. The maps obtained were analyzed using Renishaw Wire 3.2 software that incorporates a chemometrics module. Firstly, principal components analysis (PCA) was performed on the maps obtained in two spectral regions; from $1100 - 1700$ cm^{-1} denominated region I, and from $2100 - 3100$ cm^{-1} denominated region II. Graphene and perylene have overlapping Raman modes in both regions. Using a standard minimum variance value close to unity, three principal components (PC's) were identified in both data sets, and the spatial distribution of each PC is given for each spectral region in
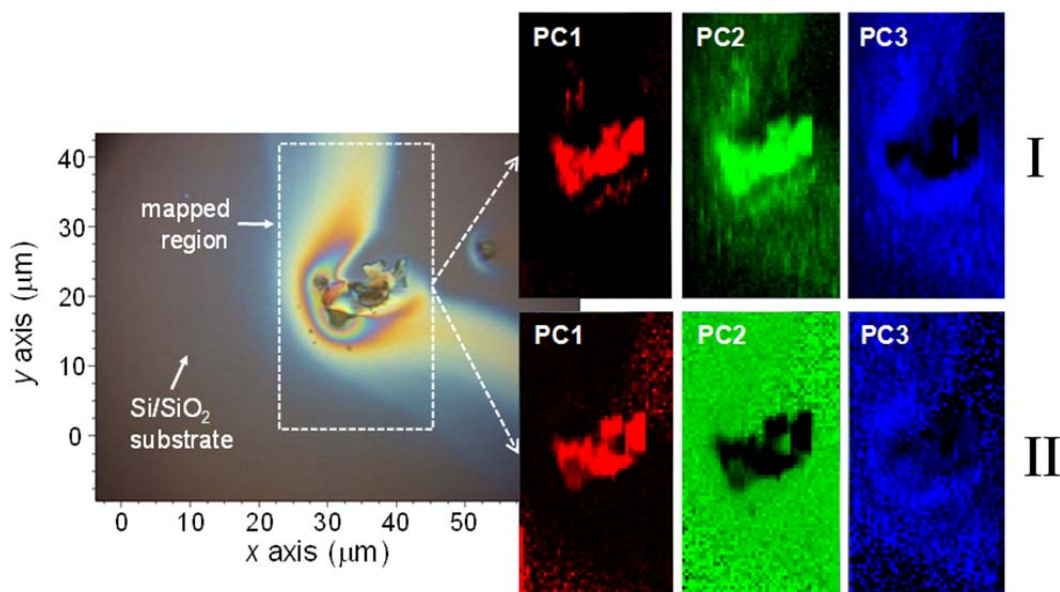
Figure S3. Visible image of PVAPery/G deposit on the Si/SiO2 substrate, and PCA images corresponding to the significant components observed for the low frequency (I) and high frequency (II) spectral regions.

In both regions I and II PC1 can be correlated to the carbonaceous flakes, and PC3 to the polymer. However, in the low frequency region I, PC2 appears to be a combination of PC1 and PC3, whereas in the high frequency region II it can be more clearly associated with the substrate. No meaningful spectral information can be extracted from the PCs since they only indicate the variance in the data. Thus, we employed the Renishaw Empty Modelling™ multivariate curve resolution – alternating least squares method (MCR-ALS) that allows component information to be rotated into physically meaningful spectral data. Figure S4 shows the 3 component maps obtained, and the average spectrum derived from the data.
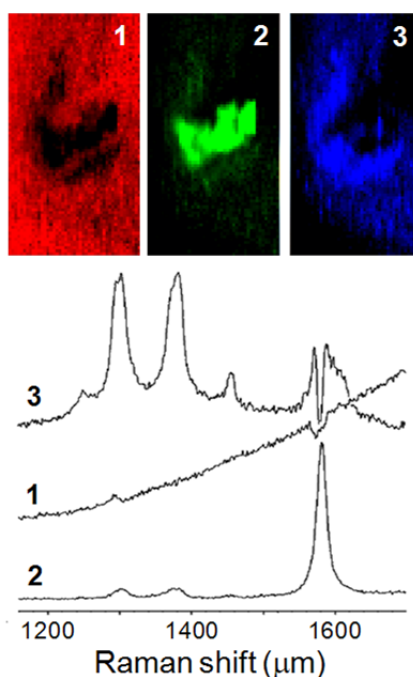
Figure S4. MCR-ALS maps from the low frequency region, and component spectra derived from the map data for the same deposit shown in Figure S3.

Component 1 appears to correspond to the strong fluorescent background observed over most of the surface, whereas components 2 and 3 clearly correspond to the position of the graphene flakes and superior concentration of PVAPery deposited on the substrate. Finally, the PVAPery polymeric surfactant surrounding the graphene can act as a vehicle for the preparation of homogeneous films. Figure S5 shows a 7 μm thick film, produced by drop casting from an aqueous solution, which is transparent and flexible.

Figure S5. Flexible and transparent film of PVAPery/G

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