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SUPPORTING INFORMATION

Understanding and optimising the packing density of perylene bisimide layers on CVD-grown graphene

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Graphene substrates – Raman spectroscopy

Representative Raman spectra of graphene after transfer to a SiO_2 substrate using the process described in the Methods section of the main manuscript and after subsequent annealing in UHV are shown in Fig. S1a. The 2D peak can be fitted with a single Lorentzian function (with a FWHM of 27 cm^{-1}) and the G:2D ratio is 1.75, both of which is characteristic for a single layer of high-quality graphene.[1] Additionally, the D peak at 1343 cm^{-1} is comparatively small and indicates a low amount of defects, confirming the high quality of the CVD graphene substrates. Virtually no change was observed in the spectrum after the annealing step to remove PMMA residue, which confirms the preservation of the good graphene quality.

Graphene intended for STM measurements was transferred onto Si/SiO_2 wafer pieces which were significantly smaller than the graphene film and draped over the edges to make contact with the conducting STM sample plate.

Figure S1b shows a large scale (300 nm x 300 nm) STM image taken of CVD graphene transferred onto 150 nm SiO_2 immediately after introduction into the vacuum and a brief anneal to just over 100°C to remove any adsorbed water. It shows some graphene wrinkles, as previously observed using AFM,[2] in the top left corner, and the graphene film following the irregular surface structure of the SiO_2 substrate in the rest of the image. The maximum observed height of graphene wrinkles was ~3 nm, whereas the roughness of the "flat" graphene/SiO_2 parts of the sample was max. 0.5 nm over the scanned area. In order to increase the contrast of smaller features like the honeycomb structure of graphene, the irregular underlying SiO_2 structure was removed by FFT-aided flattening in all high-resolution images as best as possible. Figure S4a and b show an STM image after and before image manipulation, respectively, demonstrating this process.

Perylene films on graphene – additional Raman spectra

Raman spectra of **1** on graphene show many features in addition to the characteristic G and 2D bands of the CVD graphene spectrum, as can be seen in Figures S2b and c. The two most distinct peaks characteristic for perylene compounds and originating from their core sit at 1303 cm^{-1} and 1383 cm^{-1} and can be conveniently used for mapping molecular coverage, as demonstrated in Fig. S2a. Additionally, as described in the main manuscript, the intensity ratio of these two characteristic Raman peaks of **1** and the normalized G peak at 1591(±2) cm^{-1} can be used as a measure of the packing density in the molecular ad-layer. Some additional minor peaks associated with the head groups of the dendrimers of **1** (carbonyl/carboxyl stretching vibrations) can be observed around the 2D peak of

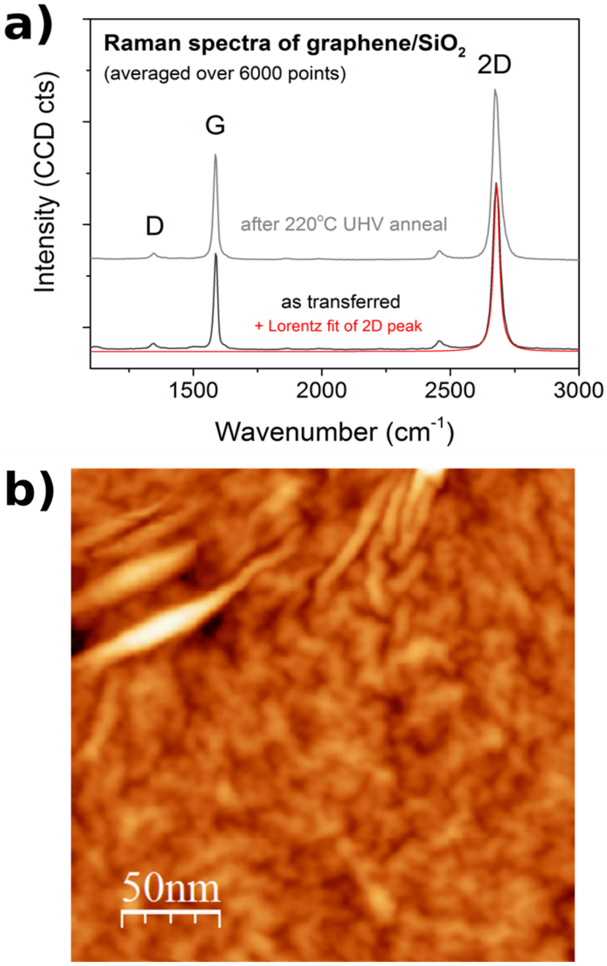

Figure S1. a) Raman spectra of a CVD-grown graphene film transferred onto SiO_2 before and after annealing, averaged over an area of 30 µm x 30 µm. b) STM image of the same graphene sample on SiO_2, taken at -1.8 V/1 nA.

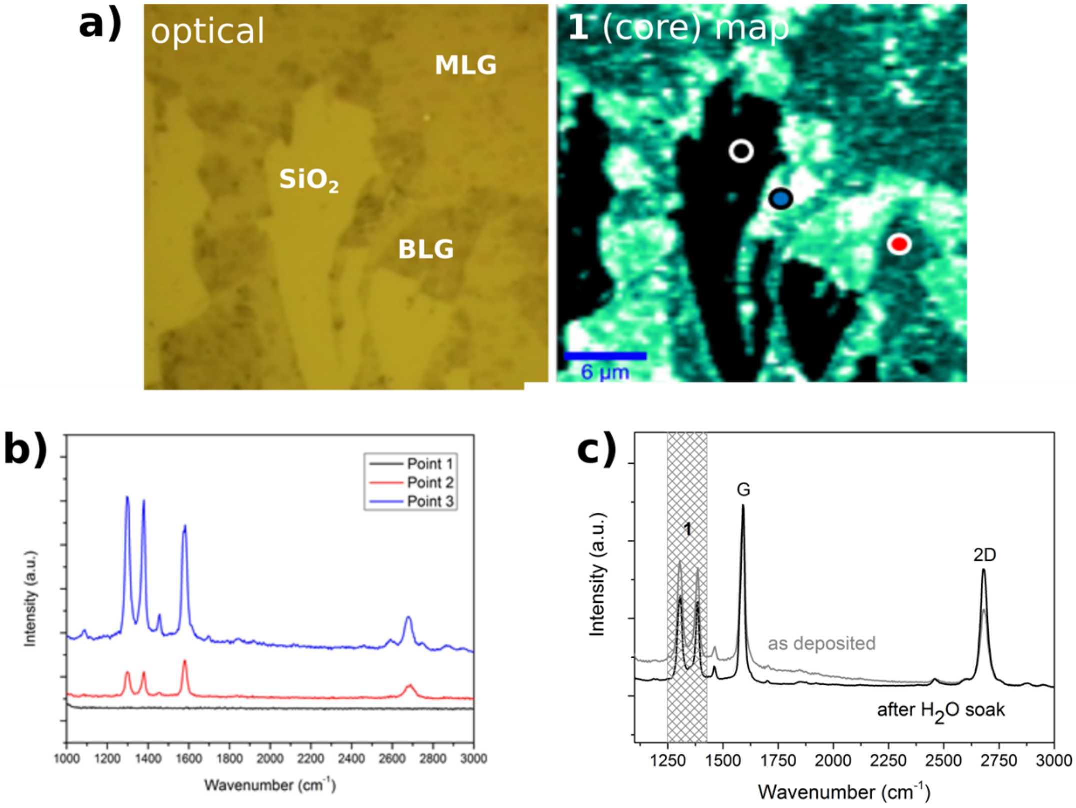

Figure S2. a) Optical image of an area of monolayer graphene/**1** (MLG/**1**) with areas of exposed SiO_2 substrate and folded over graphene/**1** (BLG/**1**) and corresponding Raman map of the characteristic peaks of **1** (see spectra below, marked area in (c)). b) Raman spectra measured at the points marked in the map in (a). c) Large area averaged (6000 pts over 30 x 30 μm^2) Raman spectra of **1** on a different graphene sample directly after deposition from aqueous solution (grey) and after soaking in H_2O for 10 minutes (black).

graphene (as shown and labeled in Figure 1b in the main manuscript) in HPD layers, but are not visible in LPD layers due to their comparatively low intensity. Figure S2a shows a map of the **1** Raman features over an area which includes both monolayer graphene as well as the bare SiO_2 substrate and folded over graphene, as can be seen in the corresponding optical image. Some points are highlighted in the map and the corresponding point spectra are shown in Fig. S2b. The Raman signature of **1** is higher in areas where the graphene/**1** layer is folded over (blue spectrum in Fig. S2b), as can be expected due to the higher density of molecules, and it is not visible at all on the SiO_2 (black spectrum), which can most likely be attributed to the lack of the enhancement effect of graphene on the Raman signal of organic molecules.[3] It should be noted that this rather defective area of a sample was chosen for display and discussion due to its many interesting features, and that the quality of the graphene/**1** films is usually much higher, without defects and with uniform coverage, as indicated in Figure 1c in the main manuscript.

It is furthermore important to discuss that **1** has another Raman peak in the immediate vicinity to the graphene G band. It is shifted by approximately -10 cm^{-1} with respect to the G peak and is visible as a shoulder for lower packing densities (*i.e.* intensities), as can be seen in the lower spectrum in Figure 1b (in the main manuscript), and as a distinguishable peak at higher packing densities. This feature must not be confused with the G band or G band splitting due to strain in the graphene.[4]

Raman spectra of **1** directly after deposition onto graphene often show a small fluorescence background and fluctuations in packing density. We attribute this to the formation of small areas of a 2nd layer or multilayers of **1**, since the inherent fluorescence of these molecules[5] is only quenched in the immediate vicinity of the graphene substrate,[6] but can be detected with the Raman spectrometer in multilayers as increased background intensity. As shown in Figure S2c, this background and therefore multilayer formation can be significantly reduced by soaking the samples in de-ionized water for at least 5 minutes.

Perylene films on graphene – Concentration, solvent choice and deposition time

The standard concentration of **1** in the aqueous buffer solution was chosen to be 0.001 mol L^{-1}, which was recommended by Backes *et al.* on the basis of their studies using **1** as a surfactant in graphene and SWCNT solutions.[7] To determine if the concentration has an impact on the adsorption characteristics, we varied it by a factor of 10 in both directions and found no difference in the Raman spectra of the thus formed molecular layers on graphene (not shown).

Additionally, we conducted a similar experiment varying the deposition time between 1 second and 20 minutes and again found no significant difference except a slight tendency towards increased multilayer formation (as evidenced by a small fluorescence background in the Raman spectrum, see Figure S2c for an example).

Aqueous buffer solution has been determined as the most suitable solvent for the deposition of **1** for a variety of reasons. Firstly, it has a comparatively low boiling point, which is desirable for wet-chemical deposition of molecules since solvent residues are minimised. Secondly, unlike other low boiling point solvents like deionised water or methanol, **1** shows very good solubility in aqueous buffer solution, which is important for the uniformity of the molecular layers on the graphene surface since it significantly reduces the formation of aggregates. Additionally, as referred to in the main manuscript, the aggregation behavior of **1** in aqueous buffer solution is very well understood while it is largely unknown for possible organic solvents like dimethyl sulfoxide, N-methyl-2-pyrrolidone or N-cyclohexyl-2-pyrrolidone. These solvents furthermore have varying levels of toxicity, which goes against the goal of easy processability that has been set for this study.

Perylene films on graphene – Details on SE measurements

As presented in Figure S3a, a six-layer optical model consisting of a Si substrate, an interface layer between Si and SiO_2, a SiO_2 layer, a graphene layer, another interface layer between graphene and perylene, and a perylene layer was built to interpret the SE spectra. A Cauchy model was used to extract the thickness of the perylene layer. The interface layer between graphene and perylene was built using an effective medium approximation (EMA) model,[8] which is composed of perylene and PMMA, considering the possible existence of PMMA residue on the graphene surface.

The perylene layer thickness was determined by fitting the experimental Ψ and Δ data with the simulated data from the optical model using a linear regression procedure. The fitting results of the Ψ and Δ data are plotted in Figure S3b and c, showing a good match between the experimental and simulated data. As mentioned in the main manuscript, the extracted thicknesses of the perylene molecule layers from this fitting procedure are 2.2 ± 0.1 nm for perylene on as-transferred graphene and 5.4 ± 0.2 nm for perylene on annealed graphene, respectively. Furthermore, the thicknesses of the interface layer between the graphene and perylene were found to be 0.6 ± 0.1 nm for perylene on as-transferred graphene and 0.2 ± 0.1 nm for perylene on annealed graphene, respectively, implying the surface roughness of the as-transferred graphene is higher than the annealed graphene most

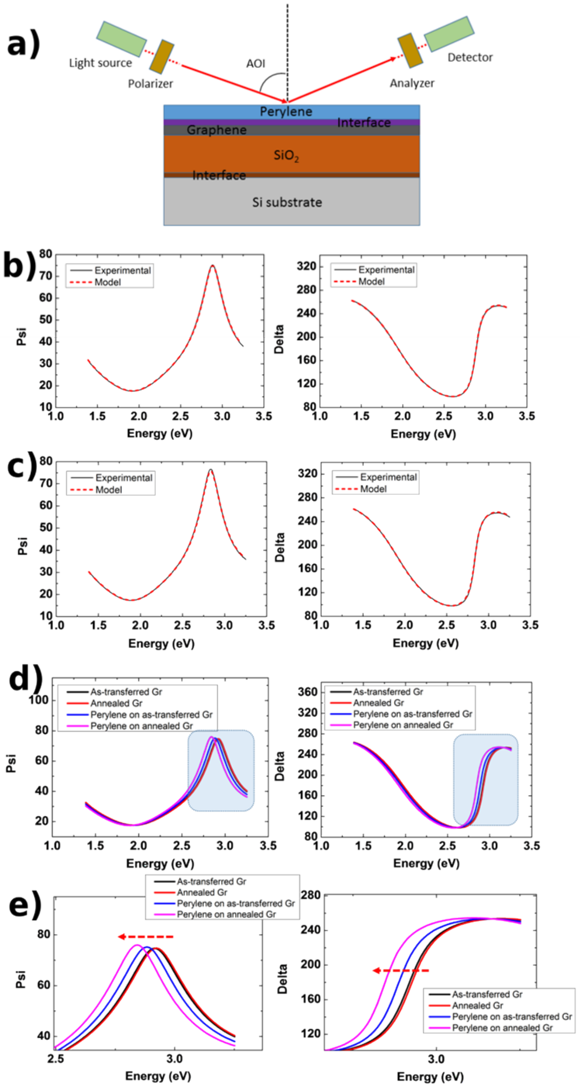

Figure S3. a) Schematic diagram of the optical model structure for SE data analysis. Fitting results of the psi (left) and delta (right) between experimental and simulated (model) data for the sample of (b) perylene on as-transferred Gr and (c) perylene on annealed Gr. (d) shows summary plots of psi and delta measured from four different samples (as-transferred Gr, annealed Gr, perylene on as-transferred Gr and perylene on annealed Gr) and (e) shows enlarged regions marked in (d).

likely due to the effect of the PMMA residue on the graphene.

In addition, comparing the measured SE spectra of four different samples which are as-transferred graphene (Gr), annealed Gr, perylene on as-transferred Gr and perylene on annealed Gr, clear peak shifts of the spectra depending on the top layer thickness change are observed in the range of 2.5 – 3.2 eV, which indicates this spectral region has a high sensitivity to the layer thickness variation of the samples.

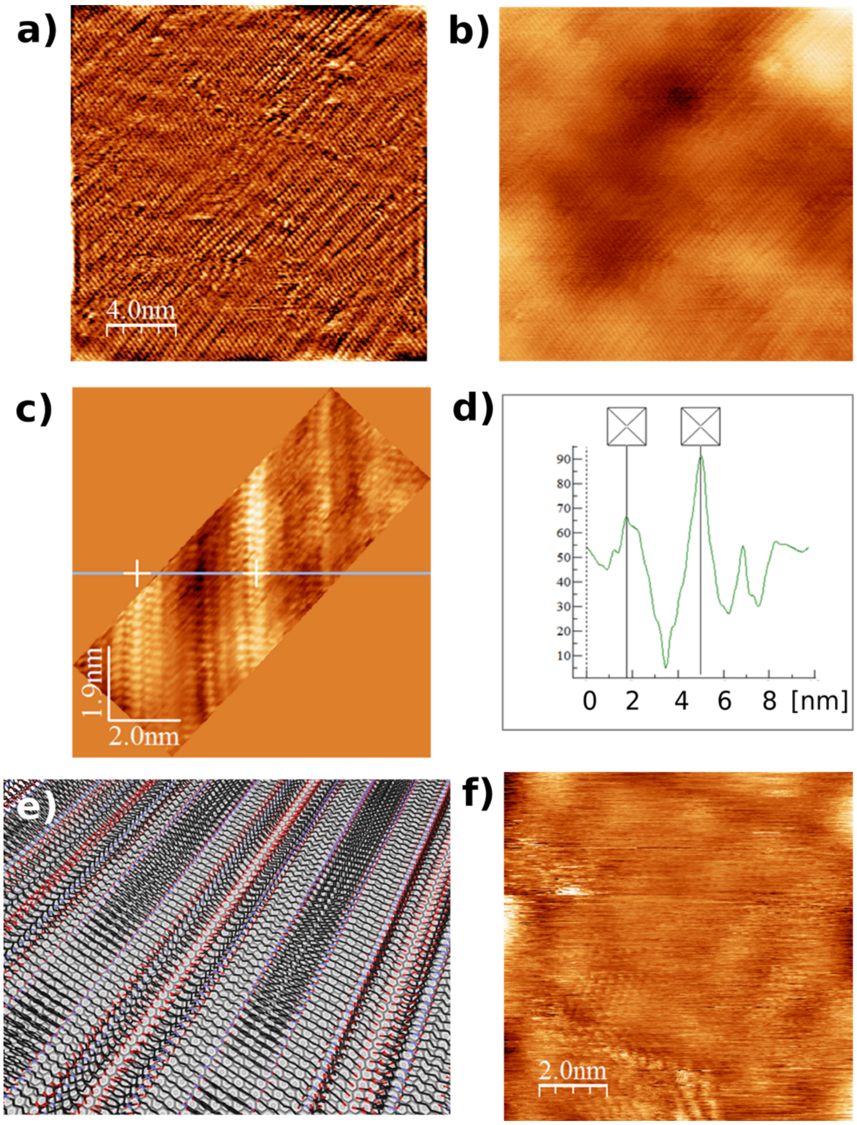

Figure S4. a) STM image of **1** on graphene/SiO$_2$ showing a large area (20 nm x 20 nm) without significant contamination or defects in the SAM; taken at -0.5 V/0.1 nA. b) The same image before processing and FFT-aided background flattening. c) High resolution STM image of **1** on graphene/SiO$_2$, taken at a lower bias (-0.3 V/0.2 nA), and rotated to align the **1** orientation with the x- and y-axes; d) profile of the y-integrated charge density along the x-axis with measurement of periodicity (i.e. molecule dimensions). e) Schematic of the high density SAM of **1** on graphene. f) Typical STM image of low density layers of **1** on as-transferred graphene/SiO$_2$, with streaky features indicating an abundance of loose material on the surface.

Perylene films on graphene – Additional STM images and analysis

As discussed in the main manuscript, STM images of high packing density SAMs of **1** could be obtained after wet-chemical deposition on a clean and pre-annealed CVD graphene film on SiO_2. Figure S4a shows an additional STM image over a large undisturbed area (20 nm x 20 nm) of the observed adsorption pattern of **1**. Figure S4b shows the same image before any FFT-aided background flattening or other image manipulation was applied. Other areas on the sample showed the same pattern in the same orientation, no other domains have been found. A schematic rendering of the proposed structure of the SAM of HPD **1** on graphene as observed by STM is shown in Figure S4e.

Figure S4c shows another high resolution STM image of **1** on graphene/SiO_2, taken at a lower bias than the other displayed ones, and rotated to align the **1** orientation with the x- and y-axes. A profile of the y-integrated charge density was taken along the x-axis and is shown in Figure S4d, including a measurement of the periodicity of the structure, *i.e.* the molecule dimensions.

Figure S4f displays a typical image obtained in the STM when attempting to image a **1** layer with low packing density, as signified by the respective Raman spectrum (not shown). As briefly mentioned in the main manuscript, the streaky features indicate loose material on the surface and prevent imaging with atomic resolution. This particular image, taken after repeated scanning of the same area, shows some areas with periodic features that could be related to the graphene substrate, but it is impossible to make any significant conclusions regarding the adsorption geometry of **1** in the low packing density layers from this or any other of the STM images taken on this surface.

Multilayers of perylenes on graphene – Fluorescence imaging and spectroscopy

Additional fluorescence images of areas with multilayer coverage of **1** on graphene are shown in Figure S5. Figure S6 displays the corresponding fluorescence spectra at different locations on the sample as well as the corresponding lifetime measurements. The latter indicate a correlation between high emission intensity and multi-exponential decay, including a long decay time component. In contrast, for low emission intensity, the decay is essentially identical to the one measured for the low packing density sample.

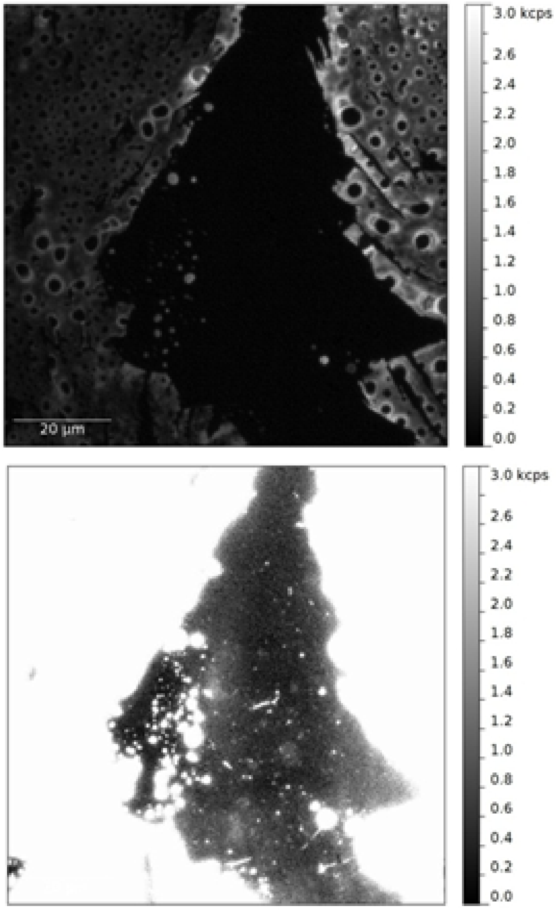

Figure S5. Fluorescence images obtained for samples with areas of multilayer coverage of **1** for two values of electron multiplying gain: 1 (upper), and 100 (lower). The lower map was taken in order to expose low-intensity areas similar to the ones visible in the image of the LPD layer in Figure 4 of the main manuscript.

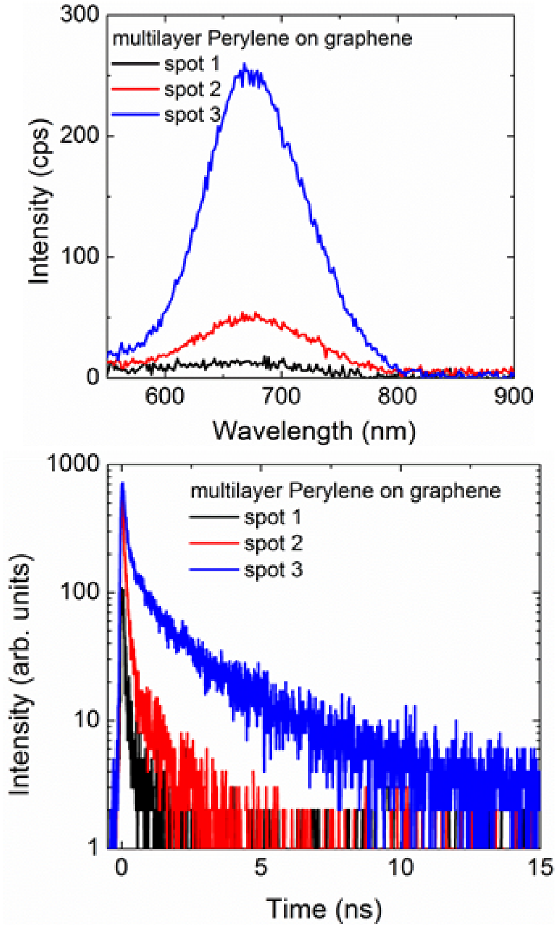

Figure S6. Upper: Fluorescence spectra obtained for a sample with multiplayer coverage of **1** on graphene for three different locations across the sample, characterized with different emission intensities. The corresponding time traces shown in the lower panel.

REFERENCES

1. A. C. Ferrari and D. M. Basko, *Nat Nano*, 2013, **8**, 235-246.
2. T. Hallam, N. C. Berner, C. Yim and G. S. Duesberg, *Advanced Materials Interfaces*, 2014, **1**.
3. E. B. Barros and M. S. Dresselhaus, *Physical Review B*, 2014, **90**, 035443.
4. T. M. G. Mohiuddin, A. Lombardo, R. R. Nair, A. Bonetti, G. Savini, R. Jalil, N. Bonini, D. M. Basko, C. Galiotis, N. Marzari, K. S. Novoselov, A. K. Geim and A. C. Ferrari, *Physical Review B*, 2009, **79**, 205433.
5. C. D. Schmidt, C. Böttcher and A. Hirsch, *European Journal of Organic Chemistry*, 2007, **2007**, 5497-5505.
6. A. Kasry, A. A. Ardakani, G. S. Tulevski, B. Menges, M. Copel and L. Vyklicky, *The Journal of Physical Chemistry C*, 2012, **116**, 2858-2862.
7. C. Backes, F. Hauke and A. Hirsch, *Advanced Materials*, 2011, **23**, 2588-2601.
8. H. Fujiwara, *Spectrocopic ellipsometry: principles and applications*, John Wiley & Sons Ltd, Chichester, 2007.