Supporting Information for

Thionine Self-Assembled Structures on Graphene: Formation, Organization, and Doping

Thiago A. S. L. de Sousa[*,†,§], Thales F. D. Fernandes[†,§], Matheus J. S. Matos[‡], Eduardo N. D. Araujo[‖], Mario S. C. Mazzoni[†], Bernardo R. A. Neves[†], and Flávio Plentz[†]

[†]*Departamento de Física, ICEx, Universidade Federal de Minas Gerais, Ave. Presidente Antônio Carlos 6627-Belo Horizonte, CEP 31270-901, Brasil*

[‡]*Departamento de Física, ICEB, Universidade Federal de Ouro Preto, R. Diogo de Vasconcelos 122, Ouro Preto, CEP 35400-000, Brasil*

[‖]*Departamento de Física, CCE, Universidade Federal de Viçosa, Avenida Peter Henry Rolfs, s/n, Viçosa, CEP 36570-900, Brasil*

[*]*Corresponding Authors:* tstephan@fisica.ufmg.br

[§]*These authors contributed equally*

Contents:

- Number of pages: 21
- Number of figures: 14
- Number of tables: 15

1- Exfoliated graphene functionalized with a 1 mM concentration solution of thionine

We functionalized two exfoliated graphene samples with a 1 mM concentration solution of thionine for 10 and 30 seconds, respectively, to elucidate how the concentration of the thionine solution affects the molecular deposition over the graphene surface.

Fig. S1 (a) shows a topography image, before functionalization, of the surface of the graphene sample functionalized for 10 seconds and Fig. S1 (b) shows this same region after functionalization with thionine. In both Figs. S1 (a) and (b) the white scale bars represent 1 μm. Fig. S1 (c) shows a topography image of the graphene surface enclosed by the white square in Fig. S1 (b). Using Gwyddion software for image processing, we made use of a mask, green areas in Fig. S1 (d), to highlight the areas over the graphene surface covered with thionine molecules, shown in Fig. S1 (c). In this way, we obtained the percentage surface coverage with thionine, 34%, that is the ratio of the highlighted area in Fig. S1 (d) to the graphene area shown in this image. In both Figs. S1 (c) and (d) the white scale bars represent 200 nm. Fig. S1 also presents the height profile of the solid white line shown in Fig. S1 (c), made in NanoScope Analysis software, as an example of the height of thionine molecules over the graphene surface, which was chosen to be at 0 nm. In order to obtain the average height of thionine relative to the graphene surface, we drew 15 height profiles (not shown) in 15 different regions of the functionalized graphene surface shown in Fig S1 (c). We obtained (1.5 ± 0.3) nm as the average height of thionine molecules over the graphene surface, which indicates that thionine lies perpendicular to the graphene sheet. The uncertainty of the mean values was obtained by the standard deviation of the 15 measured values.

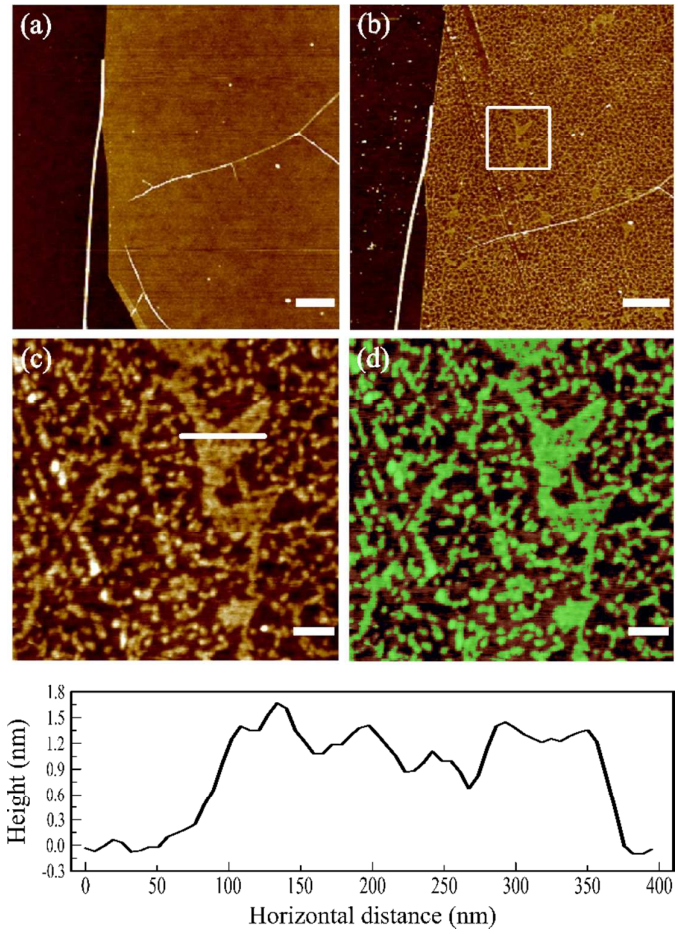

Figure S1 – Topgraphy images of the exfoliated graphene sample functionalized with thionine for 10 seconds. Image (a) shows the graphene surface before functionalization, while image (b) shows the same region shown in image (a) after the functionalization process. Image (c) shows a zoom in the area of the graphene surface enclosed by the white square, shown in image (b), and the green regions in image (d) represent the mask used to estimate the percentage surface coverage of graphene with thionine molecules. Finally, it is presented in the bottom part of the figure the height profile of the white solid line, shown in image (c). In images (a) and (b) the white scale bars represent 1 μm, while the white scale bars in images (c) and (d) represent 200 nm.

Fig. S2 (a) shows a topography image of the surface of the graphene sample before functionalization and Fig. 2 (b) shows this same region after functionalization with thionine for 30 seconds. In both Figs. S2 (a) and (b) the white scale bars represent 1 μm. Fig. S2 (c) shows a zoom in the area of the graphene surface enclosed by the white square shown in Fig. S2 (b). Repeating the same image processing used for the case presented in Fig. S1, we estimated that 83% of the surface of the graphene sample functionalized for 30 seconds is covered with thionine. Again, in both Figs. S2 (c) and (d) the white scale bars represent 200 nm. The bottom part of Fig. S2 presents the height profile of the solid white line shown in Fig. S2 (c), again made in NanoScope Analysis software, as an example of the height of thionine molecules over the graphene

surface, chosen to be at 0 nm. Once more, the average height of thionine relative to the graphene surface was obtained by drawing 15 height profiles (not shown) in 15 different regions of the functionalized graphene surface shown in Fig S2 (c). Therefore, we obtained (1.2 $\pm$ 0.2) nm as the average height of thionine molecules over the graphene surface, indicating that in this case thionine also lies perpendicular to the graphene sheet. The uncertainty of the mean values was obtained by the standard deviation of the 15 measured values.

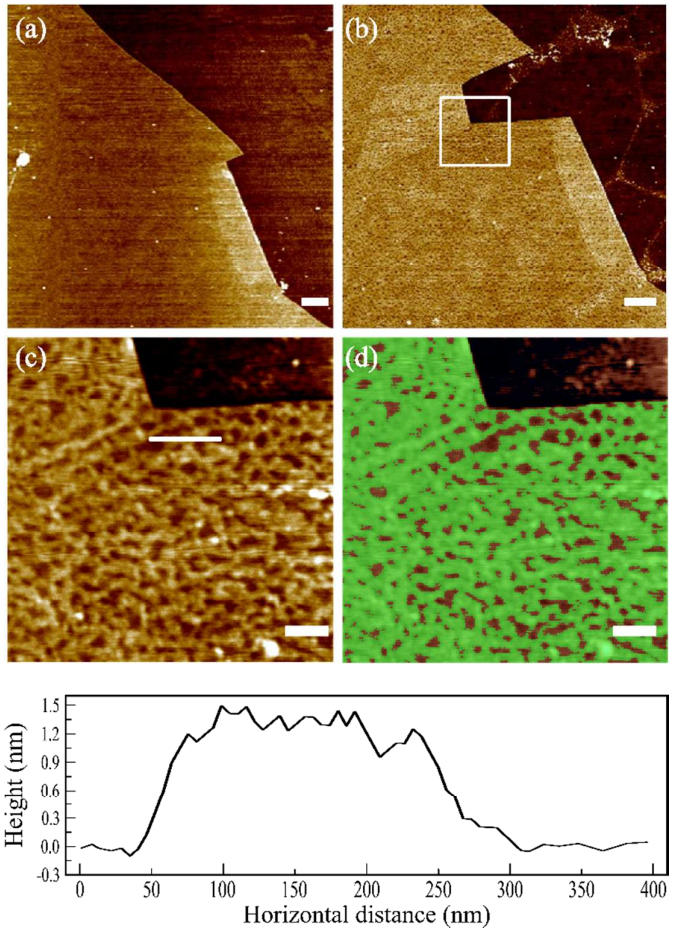

Figure S2 – Topgraphy images of the exfoliated graphene sample functionalized with thionine for 30 seconds. Image (a) shows the graphene surface before functionalization, while image (b) shows the same region shown in image (a) after the functionalization process. Image (c) shows a zoom in the area of the graphene surface enclosed by the white square, shown in image (b), and the green regions in image (d) represent the mask used to estimate the percentage surface coverage of graphene with thionine molecules. Finally, it is presented in the bottom part of the figure the height profile of the white solid line, shown in image (c). In images (a) and (b) the white scale bars represent 1 μm, while the white scale bars in images (c) and (d) represent 200 nm.

Table S1 shows the percentage surface coverage of both graphene samples functionalized for 10 and 30 seconds and shows the average height of thionine

molecules in both cases as well. Since the average height of thionine for this higher concentration of 1 mM is very close to the molecule length (1.2 nm), this is a strong indication that in this case thionine molecules lie perpendicular to the graphene surface, with no bilayer formation.

Table S1 – Percentage surface coverage and average height of thionine molecules over the graphene surface for the samples functionalized for 10 and 30 seconds.

Functionalization time (sec)	Surface coverage (%)	Thionine average height (nm)
10	34	1.5 ± 0.3
30	83	1.2 ± 0.2

2- Histograms of angles between thionine lines

The histograms of angles between thionine lines, presented in Figures 5 (a) – (e) in the main text, were obtained by the following manner. For each topographic image of graphene functionalized with thionine for 80, 90, 100, 120 and 180 minutes, shown respectively in Figures 2 (h) – (l) in the main text, we defined a reference horizontal line. So, using NanoScope Analysis software we were able to measure the angles, relative to this reference line, of several thionine filaments for each case shown in Figures 2 (h) – (l). We considered the angles relative to the reference line to increase counterclockwise.

Thus, for each image in Figures 2 (h) – (l), we measured the differences between the angle of a certain thionine line and the angles of all other considered thionine lines in order to obtain the angle between these filaments. For example, considering the angles relative to the reference line of three different thionine filaments to be θ_1, θ_2 and θ_3, we measured the differences between these angles, $\theta_1 - \theta_2$, $\theta_1 - \theta_3$ and $\theta_2 - \theta_3$, and we counted the frequency of each difference between angles, that is, the angle between a pair of thionine lines. Therefore, applying this method for the images presented in Figures 2 (h) – (l), we could plot normalized histograms of angles between several thionine lines, whose angles relative to the reference line were measured.

Figures S3 – S7 show, respectively, the topographic AFM images of graphene functionalized with thionine for 80, 90, 100, 120 and 180 minutes, shown in Figures 2 (h) – (l) in the main text. In Figures S3 – S7, the white dashed line (0º) in the bottom of each image is defined as the reference line and each of these Figures shows,

as example, the angle of three distinct thionine line (green, aqua and fuchsia dashed lines), relative to the white dashed line. Additionally, Tables S2 – S6 present, respectively, the angles of several thionine lines relative to the white dashed line drawn in Figures S3 – S7.

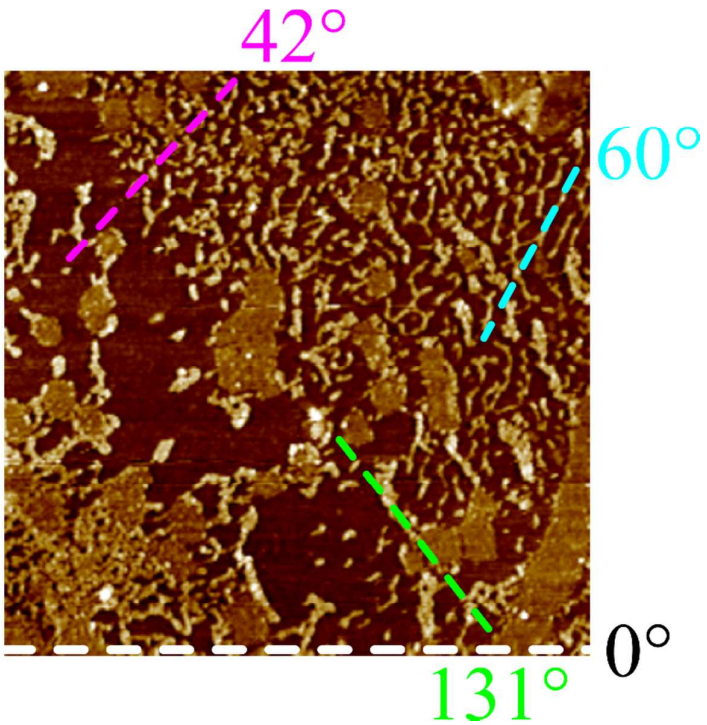

Figure S3 – Topographic AFM image of the graphene sample functionalized with thionine for 80 minutes. The white dashed line in the bottom of the image is defined as the reference line and the green, aqua and fuchsia dashed lines show, as example, the angles of three distinct thionine filaments relative to the reference line.

Table S2 – Angles of thionine filaments, relative to the reference line, for the graphene sample functionalized for 80 minutes.

80 minutes of functionalization – Angles of thionine filaments relative to the white dashed reference line											
1	61.9º	**8**	69.3º	**15**	121.9º	**22**	136.2º	**29**	66.4º	**36**	25.2º
2	62.9º	**9**	120.7º	**16**	116.2º	**23**	126.3º	**30**	136.4º	**37**	53.4º
3	59.9º	**10**	119.3º	**17**	123.7º	**24**	14.0º	**31**	47.6º	**38**	54.9º
4	76.4º	**11**	41.2º	**18**	74.9º	**25**	42.7º	**32**	59.8º	**39**	78.3º
5	23.6º	**12**	91.6º	**19**	64.1º	**26**	49.0º	**33**	74.6º	**40**	60.8º
6	79.0º	**13**	38.0º	**20**	83.5º	**27**	56.3º	**34**	132.9º	**41**	124.2º
7	88.3º	**14**	93.4º	**21**	70.2º	**28**	64.3º	**35**	105.8º	**42**	67.5º

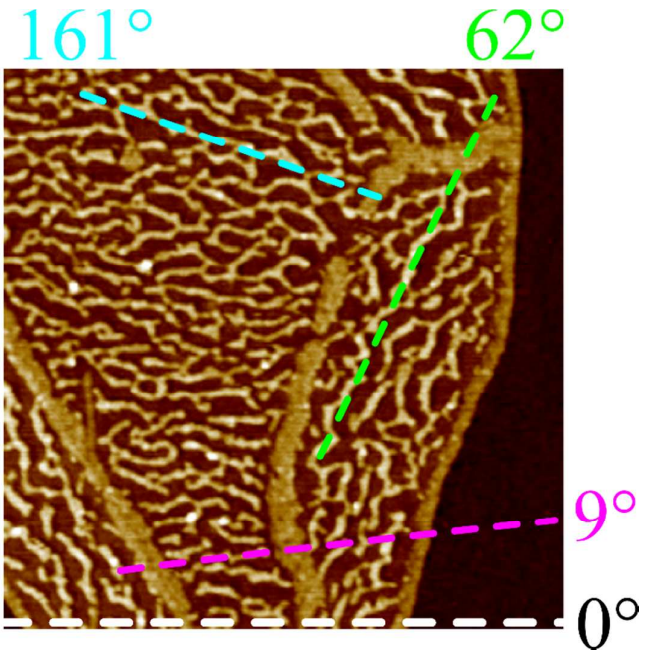

Figure S4 – Topographic AFM image of the graphene sample functionalized with thionine for 90 minutes. The white dashed line in the bottom of the image is defined as the reference line and the green, aqua and fuchsia dashed lines show, as example, the angles of three distinct thionine filaments relative to the reference line.

Table S3 – Angles of thionine filaments, relative to the reference line, for the graphene sample functionalized for 90 minutes.

90 minutes of functionalization – Angles of thionine filaments relative to the white dashed reference line											
1	54.5º	**8**	57.5º	**15**	42.6º	**22**	161.6º	**29**	153.9º	**36**	165.0º
2	59.0º	**9**	38.9º	**16**	31.2º	**23**	132.3º	**30**	153.1º	**37**	142.4º
3	37.8º	**10**	34.3º	**17**	26.3º	**24**	125.8º	**31**	150.3º	**38**	138.4º
4	46.5º	**11**	38.0º	**18**	5.6º	**25**	130.9º	**32**	166.6º	**39**	141.3º
5	36.4º	**12**	23.3º	**19**	22.2º	**26**	145.8º	**33**	155.3º	**40**	166.0º
6	45.0º	**13**	30.7º	**20**	10.3º	**27**	138.9º	**34**	156.5º	**41**	160.8º
7	54.5º	**14**	25.4º	**21**	126.7º	**28**	156.4º	**35**	154.5º	**42**	27.4º

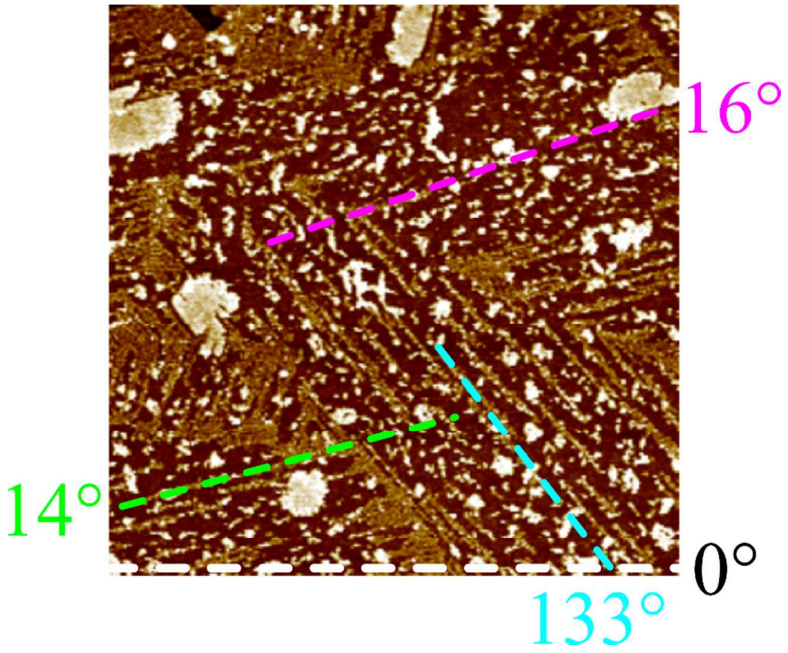

Figure S5 – Topographic AFM image of the graphene sample functionalized with thionine for 100 minutes. The white dashed line in the bottom of the image is defined as the reference line and the green, aqua and fuchsia dashed lines show, as example, the angles of three distinct thionine filaments relative to the reference line.

Table S4 – Angles of thionine filaments, relative to the reference line, for the graphene sample functionalized for 100 minutes.

100 minutes of functionalization – Angles of thionine filaments relative to the white dashed reference line											
1	11.2º	**9**	13.7º	**17**	15.0º	**25**	17.8º	**33**	133.5º	**41**	132.8º
2	14.6º	**10**	12.5º	**18**	15.1º	**26**	132.1º	**34**	134.5º	**42**	131.1º
3	16.3º	**11**	12.6º	**19**	17.1º	**27**	131.9º	**35**	130.2º	**43**	134.7º
4	14.1º	**12**	13.9º	**20**	15.1º	**28**	131.6º	**36**	131.5º	**44**	132.6º
5	13.7º	**13**	13.2º	**21**	19.2º	**29**	132.6º	**37**	134.5º	**45**	135.0º
6	13.7º	**14**	12.4º	**22**	15.8º	**30**	136.5º	**38**	131.0º	**46**	130.6º
7	13.9º	**15**	11.7º	**23**	17.6º	**31**	132.8º	**39**	133.9º	**47**	131.6º
8	13.4º	**16**	12.9º	**24**	15.7º	**32**	135.6º	**40**	129.3º	**48**	133.3º

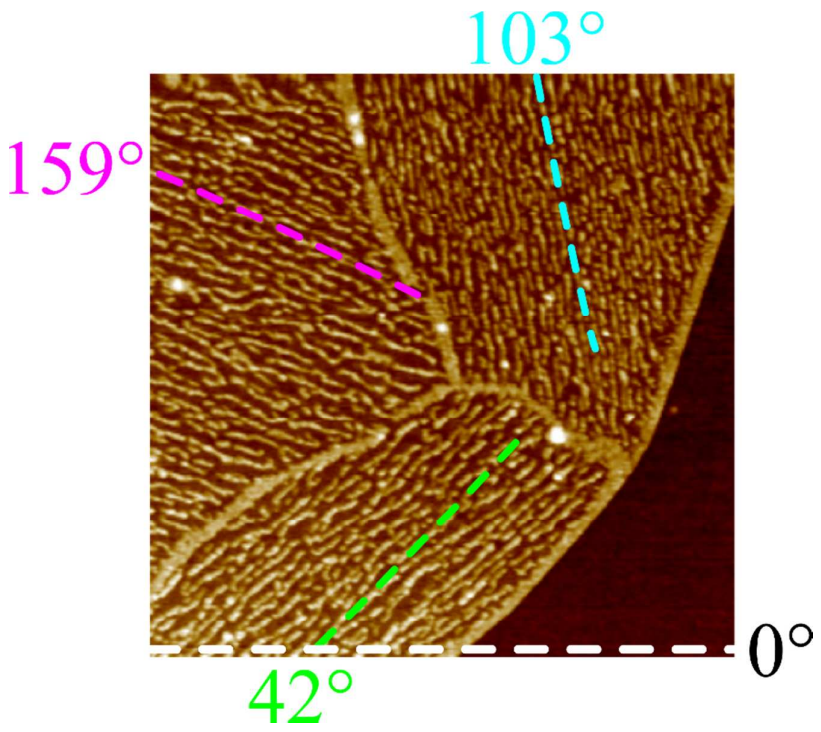

Figure S6 – Topographic AFM image of the graphene sample functionalized with thionine for 120 minutes. The white dashed line in the bottom of the image is defined as the reference line and the green, aqua and fuchsia dashed lines show, as example, the angles of three distinct thionine filaments relative to the reference line.

Table S5 – Angles of thionine filaments, relative to the reference line, for the graphene sample functionalized for 120 minutes.

120 minutes of functionalization – Angles of thionine filaments relative to the white dashed reference line											
1	159.6º	**8**	159.9º	**15**	160.2º	**22**	102.1º	**29**	104.4º	**36**	38.4º
2	157.3º	**9**	158.2º	**16**	103.3º	**23**	96.2º	**30**	104.3º	**37**	39.3º
3	158.6º	**10**	158.2º	**17**	99.3º	**24**	103.5º	**31**	40.1º	**38**	43.1º
4	157.4º	**11**	155.4º	**18**	96.8º	**25**	104.6º	**32**	38.6º	**39**	42.6º
5	155.5º	**12**	156.6º	**19**	105.6º	**26**	100.4º	**33**	42.3º	**40**	41.6º
6	156.0º	**13**	159.6º	**20**	99.9º	**27**	99.9º	**34**	39.7º	**41**	40.2º
7	156.1º	**14**	160.7º	**21**	105.2º	**28**	101.7º	**35**	38.7º		

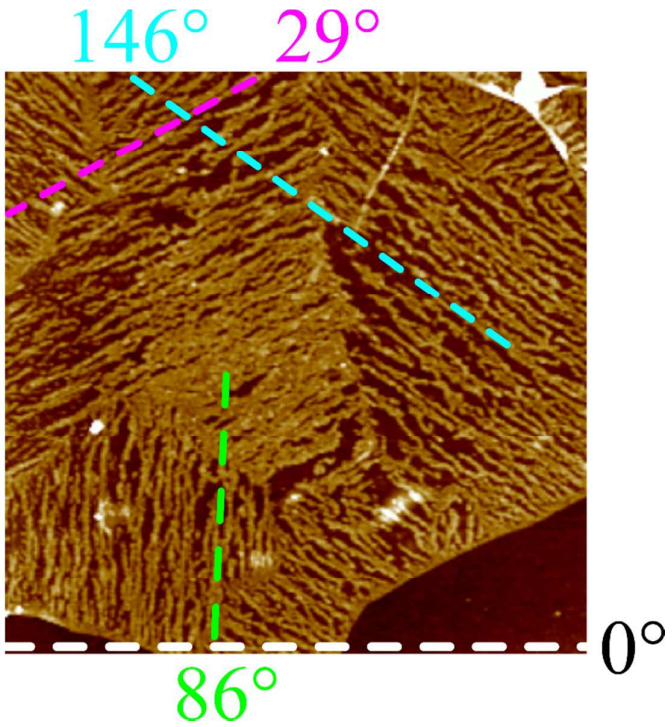

Figure S7 – Topographic AFM image of the graphene sample functionalized with thionine for 180 minutes. The white dashed line in the bottom of the image is defined as the reference line and the green, aqua and fuchsia dashed lines show, as example, the angles of three distinct thionine filaments relative to the reference line.

Table S6 – Angles of thionine filaments, relative to the reference line, for the graphene sample functionalized for 180 minutes.

180 minutes of functionalization – Angles of thionine filaments relative to the white dashed reference line													
1	150.3º	**9**	154.3º	**17**	148.7º	**25**	32.8º	**33**	33.1º	**41**	90.0º	**49**	87.3º
2	150.7º	**10**	148.0º	**18**	153.4º	**26**	29.1º	**34**	27.9º	**42**	91.8º	**50**	88.6º
3	146.3º	**11**	149.2º	**19**	150.3º	**27**	30.2º	**35**	32.9º	**43**	87.2º	**51**	90.0º
4	147.8º	**12**	147.2º	**20**	150.6º	**28**	30.6º	**36**	32.1º	**44**	89.5º	**52**	89.3º
5	147.4º	**13**	148.5º	**21**	29.9º	**29**	30.6º	**37**	28.3º	**45**	91.6º	**53**	88.6º
6	146.9º	**14**	149.3º	**22**	29.7º	**30**	32.6º	**38**	32.0º	**46**	87.5º	**54**	89.4º
7	148.0º	**15**	147.8º	**23**	31.3º	**31**	26.9º	**39**	30.3º	**47**	90.0º	**55**	89.0º
8	149.5º	**16**	150.9º	**24**	31.8º	**32**	28.4º	**40**	87.4º	**48**	90.6º	**55**	89.5º

3- Height distributions of thionine molecules over mica surface

Figure S8 (a) – (i) exhibit the height distribution (black curve), obtained by image processing in Gwyddion software, of thionine molecules over the mica samples functionalized for 2, 5, 15, 20, 30, 60, 120 and 180 minutes, respectively shown in the main text in Figures 6 (a) – (h). In order to estimate the average height of thionine molecules over mica, a normal distribution (red curve) was fitted to each one of these height distributions. The most probable value of each normal distribution is the average height of thionine molecules over mica. The uncertainties are shown as error bars in Figure 6 (i) in the main text and are given by the standard error of the mean ($\sigma_{\bar{x}} = \sigma/\sqrt{n}$), where σ is the standard deviation of the fitted function and n is the number of the performed measurements. Table S7 shows the parameters x_c (most probable value of the normal distribution), σ (standard deviation), $\sigma_{\bar{x}}$ (standard error) and R^2 (coefficient of determination) of each fitted normal distribution. In our case, n = 9, so $\sigma_{\bar{x}} = \sigma/3$. The function used to fit the height distributions is:

$$y = y_0 + \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-x_c)^2}{2\sigma^2}}$$

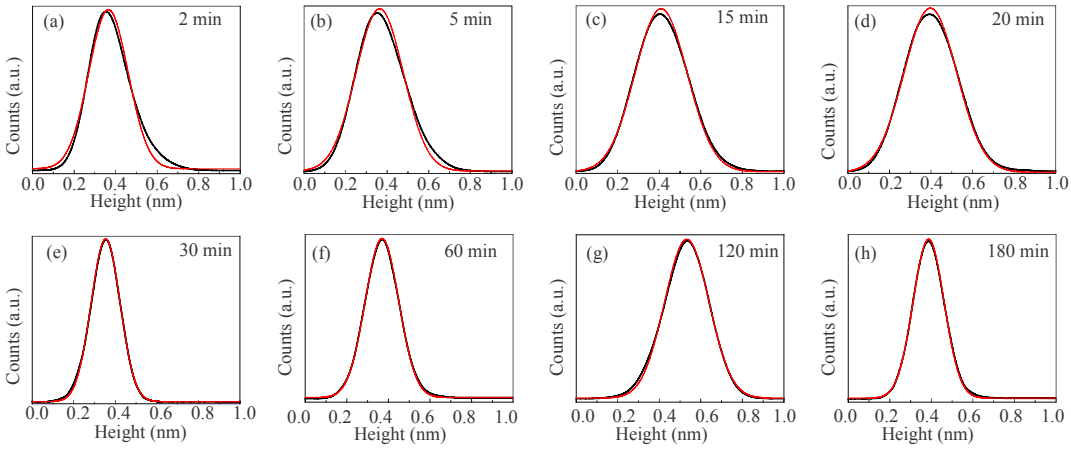

Figure S8 – Height distributions (black curve) of thionine molecules over the mica samples shown, respectively, in Figures 5 (a) – (h) in the main text. The red curve in each image represents the fitted normal distribution.

Table S7 – Most probable value ($\boldsymbol{x_c}$), standard deviation ($\boldsymbol{\sigma}$), standard error ($\boldsymbol{\sigma_{\bar{x}}}$) and coefficient of determination ($R^2 = 1$ for a perfect fit) of the fitted normal distribution respective to each mica sample functionalized with thionine.

Functionalization time (min)	$x_c\ (nm)$	$\sigma\ (nm)$	$\sigma_{\bar{x}}$	R^2
2	0.37	0.09	0.03	0.988
5	0.37	0.11	0.04	0.993
15	0.41	0.13	0.04	0.999
20	0.40	0.13	0.04	0.998
30	0.35	0.07	0.02	0.999
60	0.37	0.08	0.03	0.999
120	0.53	0.11	0.04	0.999
180	0.39	0.08	0.03	0.999

4- Electrical transport measurements performed on CVD graphene devices before and after functionalization with thionine

Our devices consist of commercial CVD monolayer graphene grown on copper foils and transferred to a 300 nm-thick SiO_2 layer, grown by dry oxidation of a low-conductivity p-type Silicon substrates. In this wafer, several 13-terminal devices were fabricated by standard photolithography and standard lift-off processes. Figure S9 (a) shows our typical CVD graphene device. The graphene Fermi level could be tuned by application of a DC voltage across the gate and the source-drain terminals, in a typical field-effect transistor configuration, as shown in Figure S9 (b). The electrodes were produced by thermal deposition of 5 nm of Cr, followed by 100 nm of Au on graphene. Finally, Figure S9 (c) shows the ohmic behavior of our devices.

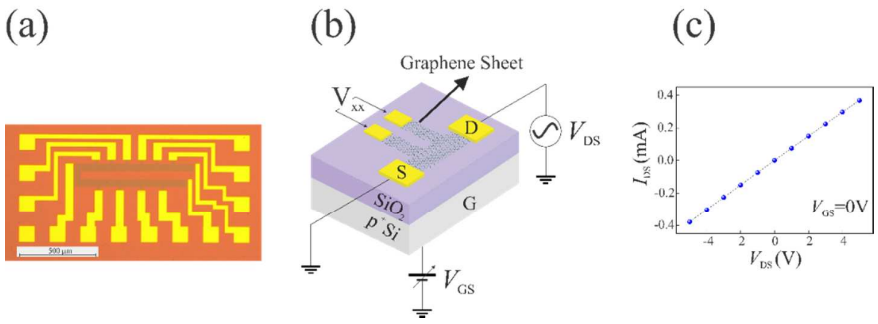

Figure S9 – (a) Optical image of our typical device used in this study. The scale bar measures 500 µm. (b) Schematic illustration of the device structure and the experimental setup used in the electrical characterization of the graphene-based FETs. The longitudinal voltage drop (V_{xx}) was measured while the gate voltage V_{GS} was swept. (c) The linear behavior of the I_{DS} *versus* V_{DS} curve shows the ohmic behavior of our devices.

Nine CVD graphene devices were functionalized with thionine (10 μM) for 2, 10, 30, 60, 80, 90, 100, 120 and 180 minutes, respectively, and Figure S10 (a) – (i) show the graphene resistivity *versus* gate voltage, V_G, before (black curves) and after (red curves) functionalization. Figure S10 (a) – (i) show that thionine promoted a significant n-type doping effect in graphene since the graphene's neutrality point (V_{NP}) in all nine devices has shifted to the left after functionalization. We were able to modulate the density of carriers n by changing the gate voltage, V_G, since $n = \alpha(V_G - V_{NP})$ and $\alpha = 7.2 \times 10^{10}\ cm^{-2}\ V^{-1}$ for a 300 nm-thick SiO_2 substrate. The electron transfer from thionine to graphene is given by $\Delta n = \alpha \Delta V_{NP}$, being ΔV_{NP} the shift of the graphene's neutrality point after functionalization. We attributed an uncertainty of ± 1 V to the shift of the graphene's neutrality point ΔV_{NP} after functionalization for each image in Figure S10. Consequently, this results in an uncertainty of $\pm$ 0.07 cm^{-2} in the electron transfer from thionine to graphene. Table S8 shows the left-shift of the graphene neutrality point ΔV_{NP}, as well as the electron transfer Δn from thionine to graphene for each functionalization time.

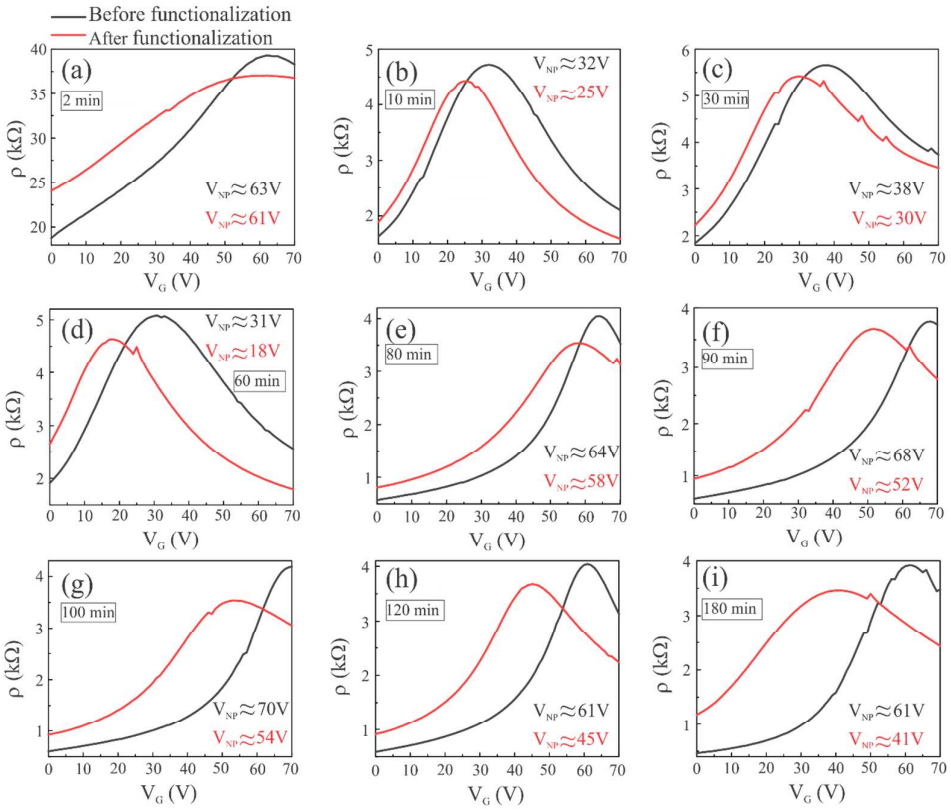

Figure S10 – (a) – (i) Graphene resistivity *versus* gate voltage before (black curve) and after (red curve) functionalization processes with thionine (10 μM) for 2, 10, 30, 60, 80, 90, 100, 120 and 180 minutes, respectively.

Table S8 – Left-shift in the position of the graphene neutrality point after functionalization with thionine (ΔV_{NP}) and electron transfer Δn from thionine to graphene for each CVD graphene device.

Functionalization time (min)	ΔV_{NP} (V)	Δn (cm^{-2})
2	2	0.14
10	7	0.50
30	8	0.58
60	13	0.94
80	6	0.43
90	16	1.15
100	16	1.15
120	19	1.37
180	18	1.30

5- Percentage surface coverage of exfoliated graphene samples functionalized with thionine

We used Gwyddion software for image processing in order to estimate the percentage surface coverage with thionine of the exfoliated graphene samples functionalized for 2, 10, 30, 60, 80, 90, 100 120 and 180 minutes, shown in the main text in Figure 2 (a), Figure 2 (c), Figure 2 (e), Figure 2 (f) and Figure 2 (h) – (l), respectively. At first, we made use of a mask, green areas in Figure S11 (a) – (i), to highlight the areas over the graphene surface covered with thionine molecules. Thus, we could estimate the ratio of the highlighted areas in Figure S11 (a) – (i) to the graphene area shown in each image. To accurately determine the percentage surface coverage of graphene with thionine molecules, we repeated this procedure of highlighting the areas covered with thionine in other topography images made in the same graphene flakes (not shown), and we evaluated the ratio of these highlighted areas to the graphene area shown in these images. Therefore, the percentage surface coverage, shown in Figure 7 (b) in the main text, is the mean value of these percentage surface coverage values obtained by image processing, whereas the standard deviation of these values represents the error bars shown in Figure 7 (b). Table S9 shows the mean value of the percentage surface coverage of graphene with thionine for each time of functionalization, and its uncertainty is given by standard deviation.

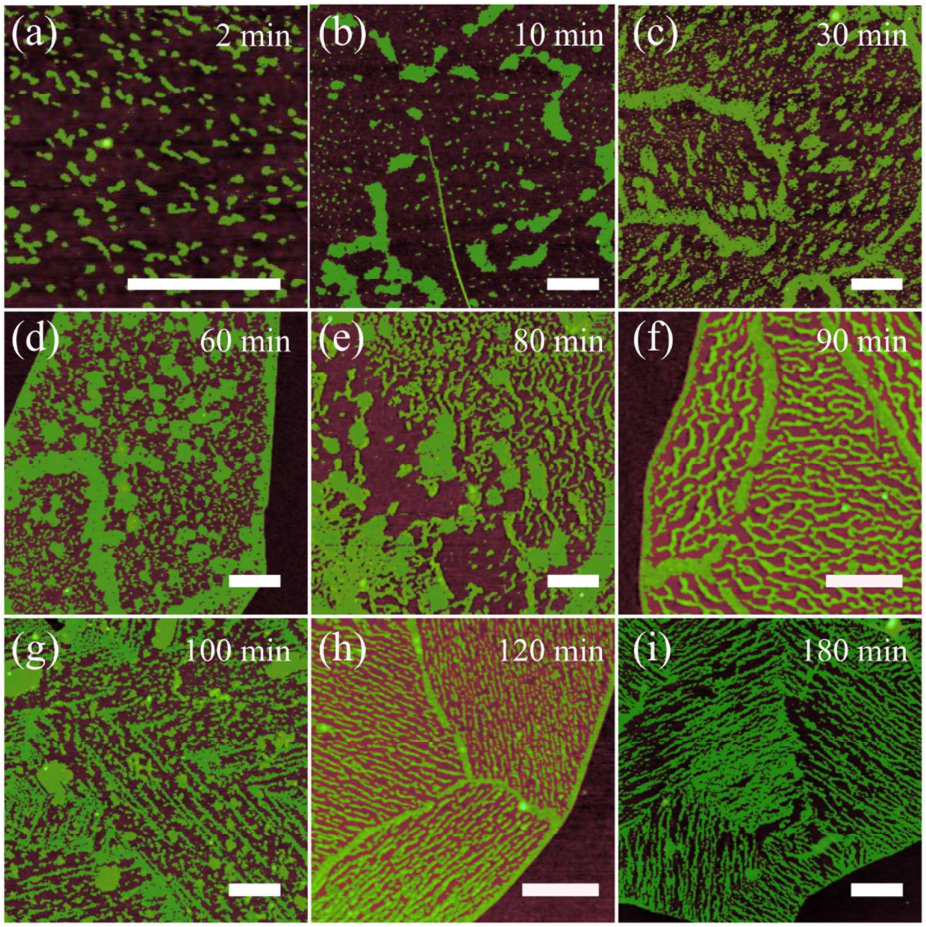

Figure S11 – Topography images of the graphene samples functionalized with thionine (10 µM). Images (a) – (i) represent, respectively, the samples functionalized for 2, 10, 30, 60, 80, 90, 100, 120 and 180 minutes. The green areas in images (a) – (i) are used to highlight the areas over the graphene surface covered with thionine molecules. In all the images above, the white scale bars represent 500 nm.

Table S9 – Mean value of the percentage surface coverage of exfoliated graphene with thionine molecules for each time of functionalization.

Functionalization time (min)	Surface coverage (%)
2	14 ± 2
10	23 ± 2
30	42 ± 2
60	49 ± 1
80	53 ± 4
90	54 ± 2
100	54 ± 2
120	52 ± 1
180	55 1

6- Raman spectroscopy of exfoliated graphene samples functionalized with thionine

We performed Raman spectroscopy investigation on five different mechanically exfoliated graphene samples, with distinct degrees of thionine adsorption, in order to provide additional evidence for doping, and also to clarify if the interaction of thionine with graphene is covalent or non-covalent.

The distinct graphene samples were functionalized, respectively, for 10, 30, 90, 120 and 180 minutes. For each sample, we took five different Raman spectra before functionalization with thionine, each one taken in a different point on the graphene flake, and we repeated this same procedure after functionalization. So, for each sample we measured the positions of the G and 2D bands of graphene for the five Raman spectra acquired before and after functionalization, and then we obtained the mean values and the uncertainties of these parameters. The uncertainty is given by the standard deviation of the five measured values of the positions of the G and 2D bands of graphene in each case. Tables S10–S14 show respectively for each functionalization time the positions of the G and 2D bands of graphene, for each one of the five Raman spectra measured before and after functionalization with thionine, as well their mean values and uncertainties.

According to Das et al., reference 46 in the main text, displacements of the G and 2D bands of graphene indicate doping, since their positions depend on the potion of the graphene Fermi level. Fig. S12 (a) and (b) show, respectively, the mean values of the positions of the G and 2D bands of graphene for each functionalization time, before and after functionalization, as well their respective uncertainties, shown as error bars. Respectively in Fig. S12 (a) and (b), the blue circles represent the mean values of the positions of the G and 2D bands of graphene before functionalization, while the red circles are related to these same parameters after functionalization. As one can see in both Fig. S12 (a) and (b) and according to Das et al., our Raman spectroscopy measurements are inconclusive regarding graphene doping by thionine, since the shifts of the G and 2D bands of graphene after functionalization are within the uncertainties of the experiment itself. In other words, the attachment of thionine molecules on graphene does not promote significant changes in the positions of both G and 2D bands of graphene in order to elucidate the type (hole or electron) and amount of charge transferred from thionine to graphene.

Therefore, in our case of low doping (see Fig. 7 **a** in the main text), Raman spectroscopy is not a versatile tool to monitor doping in graphene since a small charge transfer ($\sim 1 \times 10^{12}\ cm^{-2}$) produces only negligible shifts in the positions of the G and 2D bands of graphene.

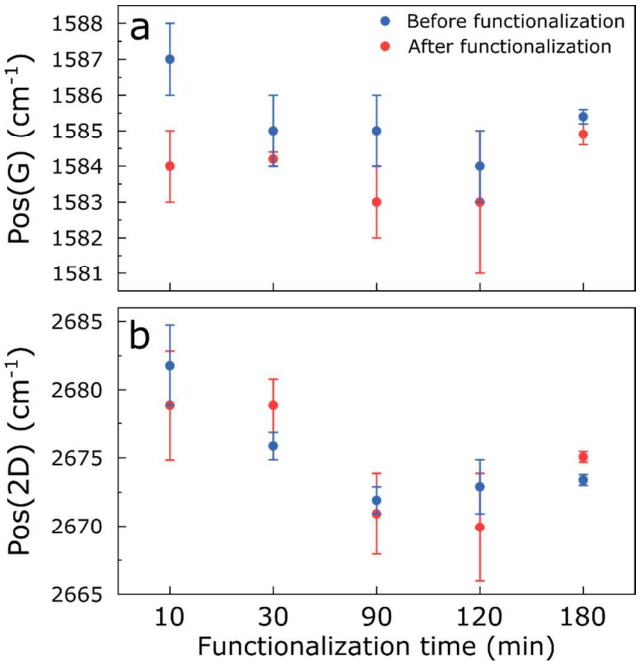

Figure S12 – Raman spectroscopy on graphene samples functionalized with thionine (10 μM) for 10, 30, 90, 120 and 180 minutes. (a) Mean values of the position of the G band of graphene before (blue circle) and after (red circles) functionalization for each functionalization time. (b) Mean values of the position of the 2D band of graphene before (blue circles) and after (red circles) functionalization for each functionalization time. In both cases, the error bars are given by standard deviation of the five measured values of the positions of the G and 2D bands of graphene, before and after functionalization, for each functionalization time.

Table S10 – Positions of the G and 2D bands of graphene for each one of the five Raman spectra measured before and after functionalization, for the 10-minute functionalized graphene.

10 minutes of functionalization	Before functionalization		After functionalization	
	Pos(G) (cm^{-1})	Pos(2D) (cm^{-1})	Pos(G) (cm^{-1})	Pos(2D) (cm^{-1})
Spectrum 1	1586.9	2686.8	1584.7	2685.4
Spectrum 2	1587.7	2679.3	1583.7	2676.2
Spectrum 3	1587.7	2678.9	1583.8	2674.9
Spectrum 4	1586.1	2683.1	1584.2	2679.4
Spectrum 5	1587.8	2680.7	1585.2	2678.4
Mean value	1587	2682	1584	2679
Uncertainty	1	3	1	4

Table S11 – Positions of the G and 2D bands of graphene for each one of the five Raman spectra measured before and after functionalization, for the 30-minute functionalized graphene.

30 minutes of functionalization	Before functionalization		After functionalization	
	Pos(G) (cm^{-1})	Pos(2D) (cm^{-1})	Pos(G) (cm^{-1})	Pos(2D) (cm^{-1})
Spectrum 1	1585.6	2675.9	1583.8	2678.3
Spectrum 2	1583.7	2675.2	1584.2	2683.0
Spectrum 3	1585.5	2675.7	1584.1	2678.3
Spectrum 4	1585.0	2674.5	1584.3	2678.3
Spectrum 5	1583.3	2676.8	1584.4	2679.1
Mean value	1585	2676	1584.2	2679
Uncertainty	1	1	0.2	2

Table S12 – Positions of the G and 2D bands of graphene for each one of the five Raman spectra measured before and after functionalization, for the 90-minute functionalized graphene.

90 minutes of functionalization	Before functionalization		After functionalization	
	Pos(G) (cm^{-1})	Pos(2D) (cm^{-1})	Pos(G) (cm^{-1})	Pos(2D) (cm^{-1})
Spectrum 1	1585.1	2673.0	1584.1	2673.7
Spectrum 2	1585.5	2673.5	1583.7	2672.5
Spectrum 3	1584.1	2670.5	1581.8	2667.3
Spectrum 4	1584.4	2672.1	1582.6	2669.8
Spectrum 5	1585.7	2672.6	1583.8	2671.7
Mean value	1585	2672	1583	2671
Uncertainty	1	1	1	3

Table S13 – Positions of the G and 2D bands of graphene for each one of the five Raman spectra measured before and after functionalization, for the 120-minute functionalized graphene.

120 minutes of functionalization	Before functionalization		After functionalization	
	Pos(G) (cm^{-1})	Pos(2D) (cm^{-1})	Pos(G) (cm^{-1})	Pos(2D) (cm^{-1})
Spectrum 1	1582.5	2671.3	1580.8	2664.2
Spectrum 2	1583.9	2673.2	1584.8	2674.1
Spectrum 3	1584.3	2672.8	1581.5	2667.8
Spectrum 4	1584.6	2674.5	1584.4	2673.4
Spectrum 5	1584.5	2674.1	1583.4	2671.1
Mean value	1584	2673	1583	2670
Uncertainty	1	2	2	4

Table S14 – Positions of the G and 2D bands of graphene for each one of the five Raman spectra measured before and after functionalization, for the 180-minute functionalized graphene.

180 minutes of functionalization	Before functionalization		After functionalization	
	Pos(G) (cm^{-1})	Pos(2D) (cm^{-1})	Pos(G) (cm^{-1})	Pos(2D) (cm^{-1})
Spectrum 1	1585.4	2673.7	1584.8	2675.2
Spectrum 2	1585.6	2673.9	1585.2	2675.9
Spectrum 3	1585.1	2672.8	1584.5	2675.0
Spectrum 4	1585.3	2673.5	1584.8	2675.0
Spectrum 5	1585.5	2673.6	1585.0	2675.1
Mean value	1585.4	2673.5	1584.9	2675.2
Uncertainty	0.2	0.4	0.3	0.4

Hutchinson et al., reference 49 in the main text, studied Raman spectroscopy of thionine on gold and reported the appearance of some Raman bands, which they attributed to thionine. The positions of these bands observed by Hutchinson et al. are quite similar to the positions of the Raman peaks shown in Fig. 8 **b** in the main text, which leads us to believe that these peaks might be attributed to thionine. Table S15 compares the positions of the Raman bands reported by Hutchinson et al. in the range of 1100 – 1800 cm^{-1} to the positions of the Raman peaks exhibited in Fig. 8 **b** in the main text as well.

Table S15 – Positions of the Raman bands reported by Hutchinson et al., reference 49 in the main text, in the range of 1100 – 1800 cm^{-1}, and positions of the Raman peaks shown in Fig. 8 **b** in the main text. Hutchinson et al. performed the Raman measurements using a 647 nm laser line, while in this report a 532 nm laser line was used.

Assignment	Thionine on gold (cm^{-1}) λ = 647 nm	Thionine on graphene (cm^{-1}) λ = 532 nm
———	———	1670
C=C	1618	1627
———	1587	———
G band	———	1583
NH_2	1500	1504
———	1480	1482
———	———	1458
C–N	1428	1428
C–N	1388	1387
———	1315	1327
C–H	1289	1289
———	———	1262
———	1224	1227

C–H	1150	1152

7- DFT calculations for different planar arrangements of thionine molecules on the graphene surface

In order to investigate more deeply if the n-type doping effect that thionine promotes in graphene depends on the molecule's relative orientation to the graphene sheet, we considered different planar arrangements of thionine on the graphene surface in DFT calculations. For this purpose, we considered five different configurations of π-stacking between graphene and a single thionine molecule, the AA, AB, Bridge 1, Bridge 2 and Bridge 3 configurations, all shown in Fig. S13. The green circles in Fig. S13 represent the thionine's carbon atoms, the blue circles represent nitrogen atoms, the yellow circles represent sulphur atoms, while the cyan circles represent hydrogen atoms. In Fig. S13, the carbon atoms in graphene sheet are represented by grey circles.

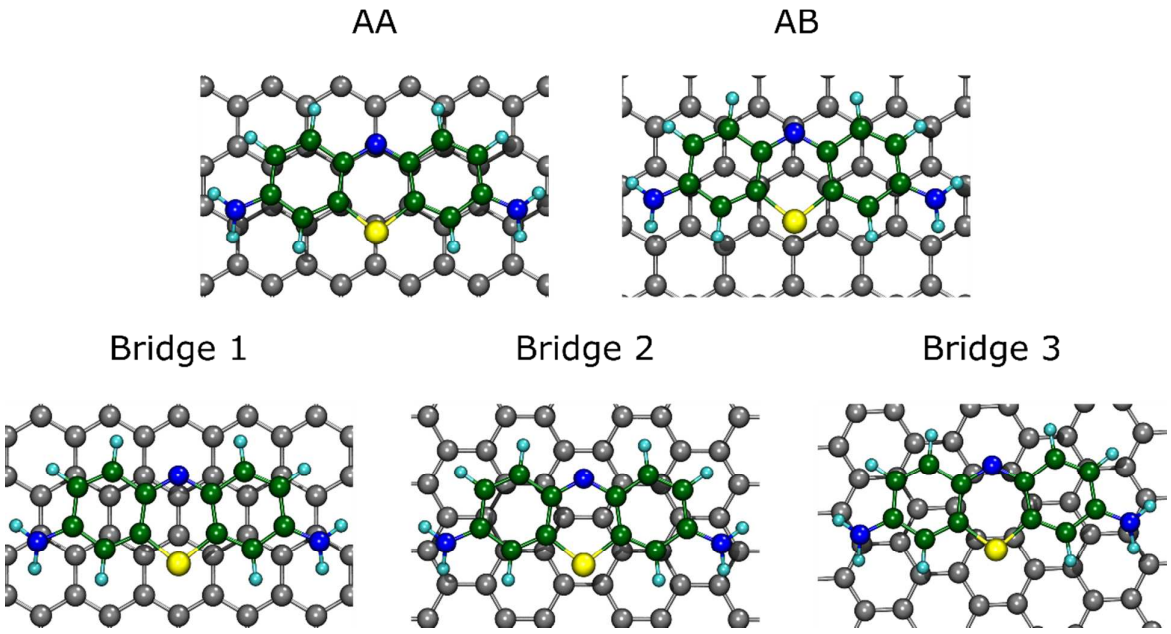

Figure S13 – Five different configurations of interaction between graphene and a single thionine molecule, AA, AB, Bridge 1, Bridge 2 and Bridge 3. Regarding the thionine molecule represented in this image, the green circles represent the molecule's carbon atoms, the blue circles represent the nitrogen atoms, the yellow circles represent the sulphur atoms and the cyan circles represent the hydrogen atoms. The carbons atoms in graphene sheet are represented by grey circles.

Fig. S14 shows the band structure of each planar hybrid system shown in Fig. S13, obtained by DFT calculations. All configurations of π-stacking between thionine and graphene considered, AA, AB, Bridge 1, Bridge 2 and Bridge 3, show a similar electron

transfer from thionine to graphene, since in these cases the Fermi level lies within the conduction band of graphene.

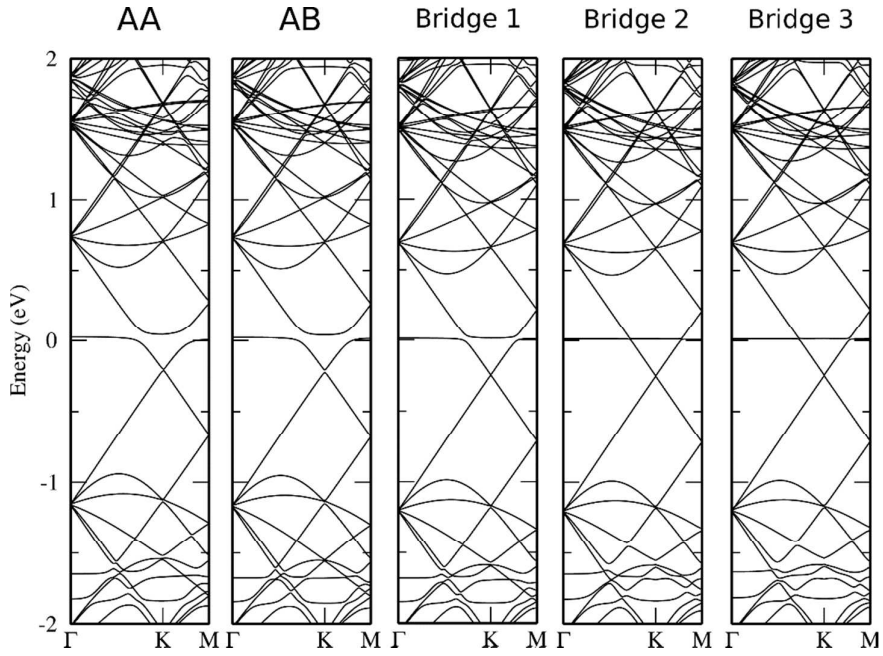

Figure S14 – Band structure of each planar arrangement of a single thionine molecule on the graphene surface, shown in Fig. S5, obtained by DFT calculations. In all configurations, the graphene Fermi level is placed inside the conduction band, which indicates an electron transfer from thionine to graphene.