Facile doping and work-function modification of few-layer graphene using molecular oxidants and reductants

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Doping of graphene is a viable route towards enhancing its electrical conductivity and modulating its work function for a wide range of technological applications. In this work, we demonstrate facile, solution-based, non-covalent surface doping of few-layer graphene (FLG) using a series of molecular metal-organic and organic species of varying n- and p-type doping strengths. In doing so we tune the electronic, optical and transport properties of FLG. We modulate the work function of graphene over a range of 2.4 eV (from 2.9 to 5.3 eV) – unprecedented for solution-based doping – via surface electron transfer. A substantial improvement of the conductivity of FLG is attributed to increasing carrier density, slightly offset by a minor reduction of mobility via Coulomb scattering. The mobility of single layer graphene has been reported to decrease significantly more via similar surface doping than FLG, which has the ability to screen buried layers. The dopant dosage influences the properties of FLG and reveals an optimal window of dopant coverage for the best transport
properties, wherein dopant molecules aggregate into small and isolated clusters on the surface of FLG. This study shows how soluble molecular dopants can easily and effectively tune the work function and improve the optoelectronic properties of graphene.

1. Introduction
The unique electrical,\cite{1,2} optical,\cite{3} mechanical,\cite{4} and chemical properties of graphene have attracted a great deal of scientific attention. Large-scale production of graphene, facilitated by chemical vapor deposition (CVD), has also resulted in significant technological interest because of its ability to yield continuous layers of either a self-limiting single-layer graphene (SLG) on copper foil\cite{5} or few-layer graphene (FLG) on a thin film of nickel.\cite{6,7} A key applied research thrust for CVD graphene is its integration as a transparent conducting electrode (TCE) in touch screens,\cite{8} optoelectronic\cite{9} and photovoltaic\cite{10,11} applications in lieu of sputtered indium-tin oxide (ITO), currently the most widely used TCE.\cite{12,13} For TCE applications, three key requirements drive materials selection: (1) low sheet resistance, (2) sufficiently high transmittance, and (3) proper energy alignment at the interface between the TCE and the active material in the device, which is generally controlled by the work function of the former. A figure of merit (FoM) for TCEs has been defined as the ratio of direct current conductivity to the optical conductivity, where a lower sheet resistance and / or a higher transmittance corresponds to a higher FoM.\cite{14} CVD graphene has outperformed graphene synthesized by any other route in the context of TCE applications, with a FoM of ca. 11 being achieved for CVD SLG; however, this value remains lower than the minimum industrial standard of FoM = 35 and more than an order of magnitude less than that of ITO (FoM = ca. 172).\cite{14} The FoM of CVD graphene can be raised through a combination of increasing the number of layers and doping. The practically attainable FoM for doped CVD graphene has been theoretically estimated to be 330, making the combination of FLG with doping a particularly promising route.\cite{8} In addition, modulation of the work function of graphene has
been intensively studied\textsuperscript{[15–19]} in order to minimize the energy barrier for charge injection between the graphene and adjacent layers and to enable both low work function cathodes or high work function anodes based on graphene in photovoltaic applications or low work function anodes in electron emission devices. This has generally resulted in enhancing the performance of graphene-based optoelectronic\textsuperscript{[18]} and photovoltaic\textsuperscript{[20]} devices and allowed for its utilization in emerging technologies such as flexible and semitransparent solar cells.\textsuperscript{[11,21,22]} FLG, which typically refers to an as-grown stack of 2-5 layers of graphene,\textsuperscript{[23]} has recently emerged as a more mechanically and chemically resilient form of graphene with demonstrated advantages over SLG,\textsuperscript{[24]} including superior performance in various applications such as gas sensors,\textsuperscript{[25]} flash memory\textsuperscript{[26]} and electrical interconnects.\textsuperscript{[27,28]} FLG electrodes exhibit only a slight variation in conductivity upon stretching and bending with full recovery to the original performance when the strain is removed,\textsuperscript{[7]} whereas the conductivity of SLG decreases significantly and irreversibly in similar conditions,\textsuperscript{[29,30]} making FLG a particularly interesting TCE candidate from the perspective of emerging applications, such as flexible electronics, optoelectronics and photovoltaics. The increased number of layers in FLG not only increases the conductivity of graphene films, but also makes them more immune to adverse effects from the substrate, such as charged impurities, and decreases the contact resistance in devices due to screening effect of the additional layers.\textsuperscript{[27,31]} Additionally, the fact that at least one graphene layer is buried in between other layers, makes FLG more robust and less prone to performance degradation due to contamination and defects during processing.\textsuperscript{[24]} Moreover, FLG is amenable to intercalation by dopants in a similar manner as graphite, which forms intercalation compounds (GIC) with small redox-active guests. The intercalated dopant molecules are thus encapsulated resulting in stable bulk doping, as has been shown with various intercalants such as Br\textsubscript{2},\textsuperscript{[32]} FeCl\textsubscript{3}\textsuperscript{[33]} and Li.\textsuperscript{[34]} Despite these advantages and opportunities, the vast majority of doping efforts reported to date have focused on SLG.
Several doping routes have been demonstrated on graphene, including deposition of alkali metals\cite{35,36} and substitutional doping\cite{37}. However, such routes generally result in an adverse effect with respect to the performance of TCEs as they tend to damage the basal plane of graphene and significantly reduce its in-plane carrier mobility.\cite{38,39} On the other hand non-covalent molecular doping, where the dopant ions resulting from electron transfer to or from the graphene are physically adsorbed on the surface of graphene without disrupting its structure, can result in an increased carrier density while minimally affecting the mobility, which results in increased conductivity.\cite{40} Additionally, use of molecules exhibiting high doping efficiency can allow for substantial benefits even with sub-monolayer coverage, thus minimally affecting the optical transmittance of the TCE, which is key to achieving a net increase of its FoM.\cite{32,41} Adding to the benefits just mentioned, considerable control over the work function of graphene can be induced by shifting the Fermi level of graphene, as a result of both addition of electrons to conduction band (n-doping) or removal of electrons from the valence band (p-doping), and the associated vacuum level shift resulting from the surface dipole produced by the electron-transfer reactions between dopant and graphene.\cite{41,42} Such modulation occurs without the sacrifice of conductivity, as has been previously reported with covalent doping routes.\cite{17}

Molecular dopants have been investigated theoretically and experimentally in the context of SLG. Examples of organic and metal-organic p-dopants that have been used include 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane, F$_4$-TCNQ,\cite{43} and molybdenum tris(1-(trifluoroacetyl)-2-(trifluoromethyl)ethane-1,2-dithiolene), Mo(tfd-COCF$_3$)$_3$ (Figure 1),\cite{41} respectively. n-Dopants include 2-(2-methoxyphenyl)-1,3-dimethyl-2,3-dihydro-1$H$-benzimidazole, MeO-DMBI,\cite{44} and the pentamethylrhodocene dimer, (RhCp*Cp)$_2$ (Figure 1).\cite{41} These species have been shown to dope SLG without disrupting its basal structure.

In this study, we investigate the solution-doping of FLG samples using the six molecular p- and n-dopants shown in Figure 1 and evaluate the extent to which the strength of the dopant
and dosage can tune the electronic, optical and transport properties of FLG and its FoM as a TCE. Our study of solution-doped FLG shows the ability to tune the work function of graphene over a very large range of 2.4 eV (between 2.9 to 5.3 eV), while improving the transport properties and FoM of FLG commensurately with the doping strength of the metal-organic molecular dopants.

2. Results

2.1. Molecular dopants used
A molecule capable of p-doping graphene by a simple one-electron redox process will have an electron affinity (EA) greater than the work function (Φ) of undoped graphene (Φ = ca. 4.43 eV). Similarly, the ionization energy (IE) of a simple one-electron n-dopant should be smaller than the work function of graphene. Accordingly, if variations in the electrostatic interactions between dopant ions and the graphene and between adjacent dopant ions are ignored, the thermodynamic strength of molecular p- and n-dopants for graphene can be approximated as EA(dopant) − Φ(graphene) and Φ(graphene) − IE(dopant), respectively, where a larger positive value in each case indicates a stronger dopant. The six dopants used in this study are shown in Figure 1. However, since the doping is carried out in solution and since solid-state EA/IE values have not been determined for all six compounds (and, in any case, would not be appropriate for the two n-dopants, which, as discussed below, are not simple one-electron reductants), we define the dopant strength using the solution redox potentials of the molecular dopants; Figure 1 plots these potentials vs. ferrocenium/ferrocene (FeCp₂⁺/0). As well as redox potential, dopants were also selected considering molecular size and shape; dopants forming large three-dimensional molecular ions were selected where possible in order to minimize Coulombic interactions between contributed charge carriers and dopant ions and to minimize π interactions between dopants and graphene. For example, the 2D F₄-TCNQ was not included in the present study. Instead, three molybdenum
tris(dithiolene) derivatives Mo(tfd-COCF$_3$)$_3$, Mo(tfd-CO$_2$Me)$_3$, and Mo(PhBz-dt)$_3$ were used as p-dopants; these compounds resemble molybdenum tris[1,2-bis(trifluoromethyl)ethane-1,2-dithiolene], Mo(tfd)$_3$, which has been used as a vacuum-processable dopant for organic semiconductors that shows less tendency to diffuse within organic films than F$_4$-TCNQ,[45,46] but their different substituents lead to increased solubility and allow their reduction potentials to be varied from +0.39 to −0.38 V (a range that includes the reduction potential of F$_4$-TCNQ). Mo(tfd-COCF$_3$)$_3$ has, as noted above, previously been used to dope SLG,[41] Mo(tfd-CO$_2$Me)$_3$ has been used for the solution doping of poly(3-hexylthiophene),[47] and Mo(PhBz-dt)$_3$ is a new compound (see experimental section). In addition, tris(4-bromophenyl)ammoniumyl hexachloroantimonate (Magic Blue), was selected to extend the range of redox potentials to +0.70 V.[48] Magic Blue has also been used as a p-dopant for organic semiconductors[49] and has recently been demonstrated to raise the work function of trilayer MoS$_2$ by 0.8 eV,[50] and SLG (up to 5.1 eV) for application in mid-infrared hyperbolic metamaterials.[51] Unlike the other dopants examined, Magic Blue is a salt of an oxidizing cation and its use is anticipated to result in formation of neutral tris(4-bromophenyl)amine, which is expected to be washed away from a substrate during rinsing, leaving SbCl$_6^-$ counterions on the doped surface.[48,50] Strong one-electron molecular n-dopants necessarily have low IE and so can be highly air sensitive. The n-dopants used in this work –pentamethylrhodocene dimer, (RhCp*Cp)$_2$ and ruthenium (pentamethylcyclopentadienyl)(mesitylene) dimer, (RuCp*mes)$_2$ – are not simple one-electron reductants; these compounds react with oxidants to form the corresponding monomeric cations; the potentials for this reaction (both ca. −2 V), shown in Figure 1, are obtained according to:

$$E(M^+/0.5M_2) = E(M^+/M) + ΔG_{Diss}(M_2)/2F$$

(1)

where $E(M^+/M)$ is obtained from the cyclic voltammetry (CV) of the corresponding monomer cation and $ΔG_{Diss}(M_2)$ is estimated from DFT calculations.[52] This coupling of electron-transfer and bond-cleavage processes results in materials that are moderately air...
stable, despite their strongly reducing character. Both of these compounds have been used as dopants for organic semiconductors\[53–55\] and for reducing the work function of oxide electrodes.\[56,57\] Pentamethylrhodocene dimer has also been recently demonstrated to dope SLG, causing the work function to decrease by 1.29 eV.\[41\]

The hypothetical potential corresponding to the work function of pristine FLG, determined to be 4.43 eV in this work, is represented by a gray box in Figure 1, the vertical height of which represents experimental uncertainties in determining the absolute potential of FeCp₂⁺/₀ relative to vacuum.

### 2.2. Surface coverage of dopants on few-layer graphene

Doping was achieved by immersing FLG on glass in dichloromethane (Magic Blue) or toluene (other dopants) solutions of the dopant for multiple durations (more detail is given in the experimental section). The immersion allows for dopant-induced electron transfer at the surface, which is anticipated to produce charged dopant ions adhered to the oppositely charged FLG surface, but can also potentially result in the strong physisorption of neutral species, which would not contribute to the carrier density. Subsequent rinsing of the substrate is expected to remove weakly physisorbed neutral dopants, but, depending on the strength of dopant-graphene interactions some more strongly unreacted material may remain (as seen for example in SLG heavily n-doped with (RhCp*Cp)₂).\[41\]

For the molybdenum-based p-dopants, the doping step does not result in a change in dopant composition. With Magic Blue, however, the hole injection to the graphene neutralizes the ammoniumyl species which, no longer coulombically bound to either the FLG surface or the hexachloroantimonate counterion, can leave the adhered anion behind. For the n-dopants, the initial doping of the graphene results in the decoupling of dimers followed by a second reduction, but with no net change in atomic composition.
X-ray photoelectron spectroscopy (XPS) was used to determine dopant surface coverage; the results are shown in Table S1. Integrating the expected signal attenuation due to the inelastic scattering of photoelectrons from the C 1s and Si 2p ionizations allows us to estimate the effective thickness of the FLG on the glass substrate, which typically gives a thickness corresponding to 8-10 layers. Adjusting the C 1s intensity for the number of layers and assuming a uniform FLG thickness, we can estimate the surface coverage of dopants using the atomic ratio of $M/C_{\text{graphene}}$, where M is an element exclusive to the particular dopant. The methodology of these calculations is described in more detail in the supporting information.

For all the dopants examined, surface coverage increases with immersion time, although the number of dopants per unit area of FLG shows strong dopant-to-dopant variability. For example, the weak dopant Mo(PhBz-dt)$_3$ is deposited to afford a coverage of 0.212 Dopants/nm$^2$ after 180 minutes, while the slightly stronger dopant Mo(tfd-CO$_2$Me)$_3$ only yields 0.0363 Dopants/nm$^2$ after the same time period. In this particular comparison it is likely that there is some physisorption of neutral species for the weaker dopant (as suggested by UPS data, see below), perhaps due to interactions between its phenyl substituents and the surface. More generally, for most of the dopants, the XPS data do not enable us to reliably determine the redox state of the dopant and so the relative contributions of neutral and ionic species to the observed surface coverages. However, in the case of Magic Blue, the XPS clearly shows only the elements from the SbCl$_6$ counterion and no evidence for any cationic or neutral N- and Br-containing oxidant, suggesting that the Sb coverage can be equated to the number of electrons removed from the graphene. It is worth noting that there is significant discussion in the literature of the distinction between the level of hole or electron transfer to a material and the number of free carriers that are actually generated. Several studies suggest that the free-carrier concentration is substantially lower than would be expected based solely on the number of holes or electrons that appear to have been injected into a material as judged by quantification of the number of compensating ions that would be associated with those
Therefore, care must be taken when comparing carrier concentrations determined by measurement of electrical properties of the materials to those that one could simplistically infer by assuming one free carrier being injected per compensating ion. The importance of this distinction will become more apparent below.

2.3. Electronic properties of solution-doped few-layer graphene

Ultraviolet photoelectron spectroscopy (UPS) was used to measure the changes in FLG work function upon solution-doping. In Figure 2a, we show the secondary electron cut-off (SEC) of pristine FLG and solution-doped FLG for 60 min (moderate exposure and optimal conditions for transport measurements, as will be shown in section 2.4). The SEC shifts to a lower binding energy for p-dopants where the graphene valence band is expected to be depopulated as a result of electron transfer to the dopant molecules (or, in the case of Magic Blue, molecular cations), whereas the opposite trend is observed for n-dopants with electrons transferring from the dimeric dopants into the graphene conduction band. The electron transfer in doped FLG is evident from the shift in carbon core level (C 1s) measured using XPS as shown in Figure 2b for p-doped FLG, where the peak shifts to a lower binding energy. The peak shift is due to lowering of the Fermi level of graphene into its valence band as a result of electrons being transferred to the p-dopants, which causes the core levels to appear at a lower binding energy. The shift in the C 1s peak increases with the increase of the dopant strength as shown qualitatively in Figure 2b and more quantitatively in Figure S1. The data show a good correlation between the Fermi-level shift and the p-dopant redox potential, as expected.

The work function, \( \Phi \), was calculated from the measured SEC \( (\Phi = 21.22 \text{-SEC}) \) for all samples and is shown in Figure 2c, along with the work function of pristine FLG \( (\Phi = 4.43 \text{ eV}) \). Generally, we find that the shifts in \( \Phi \) are larger with increasing dopant strength, consistent with expectations that more electrons will be transferred if the difference between

\[ \text{charges.} \]
the redox potential energy of the dopant and the $E_F$ of graphene is larger.\textsuperscript{[19]} For Mo(PhBz-dt)$_3$, the XPS data suggests a much greater surface coverage than for the other Mo p-dopants, despite its weaker dopant strength and in apparent contradiction to the observed work function shifts. Presumably, this dopant absorbs relatively strongly to graphene in its neutral form, as well as an anion. The work function of FLG was increased by up to 0.6 eV for the strongest p-dopant (Magic Blue) and decreased by 1.5 eV for the strongest n-dopant (RuCp*mes dimer), which to the best of our knowledge, is the largest work-function shift reported to date for solution-based doping of graphene.\textsuperscript{[41]} Overall the work function of graphene can be tuned over a broad range of 2.1 eV from 2.9 eV to 5.0 eV using this moderate exposure time. The results reported thus far pertain to a solution-doping time of 60 min. Extending the exposure time further increases the dopant coverage, as evidenced by the increase in the intensity of the dopant-related XPS peaks shown in Figure S1. These lead to additional shifts of the work function which, however, appear to be minor and dopant-dependent. In Figure 2d, we have plotted the work function of p-doped FLG for solution-doping times of 60 min and 180 min (extended exposure). The shift seems to increase with dopant strength and appears to be more pronounced in the case of Magic Blue, where the total shift of 0.83 eV after 180 min is considerably higher than the 0.6 eV shift observed at 60 min. The change in work function of doped graphene can result from a Fermi level shift due to the change in the band population resulting from electron-transfer reactions\textsuperscript{[15,19,60]} and/or from a vacuum level shift due to formation of surface dipoles, as will be discussed in more detail in the Discussion section.\textsuperscript{[41,42]} We have compared the changes of the work function (Figure 2d) and the shifts of the sp$^2$ component of the C 1s peak measured by XPS (Figure S1) for FLG p-doped for 60 and 180 min. The shifts in the XPS core level (correlated to the Fermi level shift) are smaller than the observed changes in the work function and are not affected significantly by prolonging doping time, indicating that the vacuum-level shift dominates the work function shift at longer exposure times, consistent with previous studies. The extended exposure time
expands the work-function window achievable for graphene to a very large value of 2.4 eV (from 2.9 to 5.3 eV).

The unique electronic structure and underlying phonon-electron resonant Raman scattering processes in graphene make the position, intensity and full width at half maximum (FWHM) of its Raman bands sensitive to the presence of dopant molecules and to changes in the charge-carrier density. Raman spectra of pristine and p-doped FLG (60 min) are shown in Figure 3a, showing the two characteristic peaks of graphene, namely the G-peak around 1580 cm\(^{-1}\) and the 2D-peak centered around 2750 cm\(^{-1}\). The G-peak results from the lateral stretching of carbon atoms involving the E\(_{2g}\) in-plane optical phonon mode near the Γ point. The 2D-peak results from a resonant Raman process involving two phonons, and is the overtone of the D-peak (1375 cm\(^{-1}\)) which originates from a second-order process of one phonon near the K point and one defect.\(^{[61]}\) Though the D-peak requires the presence of a defect for its activation in graphene, its overtone (2D-peak) is always present, with its shape and position reflecting the electronic structure and hence the number of layers in graphene. The Raman spectra of p-doped FLG show a shift in the position of the G-peak and 2D-peak towards a higher energy, in agreement with previous results on electrical,\(^{[62]}\) electrochemical,\(^{[63]}\) and chemical\(^{[64]}\) p-doping of graphene. The G-peak of doped graphene always shifts to a higher energy regardless of the type of induced carriers due to the non-adiabatic removal of the Kohn anomaly from the Γ point, while the 2D-peak shift direction depends on the type of doping, where p-type doping causes a shift towards higher energy due to lattice contractions caused by the withdrawal of electrons from graphene.\(^{[63]}\)

In Figure 3b and 3c we show the Raman shift of the G-peak and 2D-peak, respectively, for pristine and p-doped FLG. For the determination of these Raman shifts, the G-peak was fitted with a single Lorentzian line shape, while the 2D-peak was fitted with two Lorentzian components, a high-energy peak denoted as 2D\(^{H}\) (ca. 2746 cm\(^{-1}\)) and a low-energy peak denoted as 2D\(^{L}\) (ca. 2712 cm\(^{-1}\)). We observe that the position of 2D\(^{H}\) appears to be insensitive
to doping, in contrast to 2D\textsuperscript{L}, the position of which generally shifts to higher energy as shown in Figure 3c (See Figure S2 for more information). The shift in the position of the G-peak is correlated with the strength of the dopant, as shown in Figure 3b. The largest shift (1.75 cm\textsuperscript{-1}) is observed for FLG doped with Magic Blue. In addition to the energy shift of the G-peak and 2D-peaks, the intensity ratio I(2D)/I(G) decreases (Figure S3) with doping, as has been previously reported for doped FLG.\textsuperscript{[64]}

The doping of SLG has generally resulted in significantly larger shifts as compared with FLG. For instance, doping SLG with Mo(tfd-COCF\textsubscript{3})\textsubscript{3} yielded a shift of ca. 10 cm\textsuperscript{-1},\textsuperscript{[41]} an order-of-magnitude greater than when doping FLG (this work). The small shift of G-peak was recently interpreted as a lower degree of charge transfer (weaker doping effect) in FLG as compared to SLG.\textsuperscript{[65]} We believe this interpretation may be inaccurate. FLG in this work shows a strong doping effect, as indicated by large shifts in work function and further substantiated by transport measurements in the next section (see below). Instead, we attribute the weak shift of the G-peak to the fact that the Raman signal is a superposition of all layers of the FLG, whereas doping is expected to take place solely on the top-most exposed 1 or 2 layers and is not expected to affect the bulk of the FLG sample as the charge transfer is screened by the neighboring sheets. The stiffening of the G-peak resulting from the transfer of charge carriers to/from the top layers is counteracted by the pristine G-peak signals coming from the bulk. This is supported by the observed increase in the FWHM of the G-peak shown in Figure S3.

2.4. Transport properties of solution-doped few-layer graphene

Next, we investigate the influence of molecular doping on the transport properties of FLG. The average sheet resistance of pristine FLG measured in our lab is 917 ± 66 Ω/□. As expected, it generally decreases upon both n- and p-doping (Figure 4a), although the weaker p-dopants Mo(tfd-CO\textsubscript{2}Me)\textsubscript{3} and Mo(PhBz-dt)\textsubscript{3} have minimal effects. The drop in sheet resistance correlates well with the strength of the dopant for both dopant types. The lowest
values were observed for p-dopant Magic Blue, reaching a value of 403 ± 35 Ω/□, while it was 427 ± 9 Ω/□ for the n-dopant (RuCp*mes)$_2$. We compare the FoM of the pristine and doped FLG in Figure 4b. The FoM nearly doubles for both the strongest p-dopant (Magic Blue) and the strongest n-dopant ((RuCp*mes)$_2$). The increase of FoM is attributed to the significant decrease in the sheet resistance at the cost of only 8% reduction in transmission as compared to the pristine sample (as shown in Figure S4).

To elucidate the factors influencing the changes in sheet resistance, we have performed Hall effect measurements. These measurements were performed in air; however, the Van der Pauw conductivities determined were very similar to those from the linear four-point probe measurements conducted in inert atmosphere (see Table S2); thus, we believe that the Hall effect results are not significantly affected by the reactivity of doped graphene with oxygen or water. We confirm the type of doping through the sign of the Hall coefficient (shown in Table S3), which is then used to deduce the charge carrier density and subsequently the Hall mobility. In Figure 4c, we plot the charge-carrier density of solution-doped FLG samples, where it is observed to consistently increase with increasing dopant strength in agreement with the trend of reduced sheet resistance. Pristine FLG exhibits p-type characteristics with a carrier concentration of ca. $3 \times 10^{13}$ cm$^{-2}$ and a mobility of 266 cm$^2$/Vs. The characteristics of p-type doping of as-prepared graphene have been previously observed, and have been linked to unintentional hole doping due to PMMA residues from the transfer process, in addition to environmental contamination.$^{[66]}$ The measured mobility of pristine CVD FLG is consistent with values reported for CVD graphene,$^{[67,68]}$ and is significantly lower than in mechanically exfoliated graphene,$^{[69]}$ due to the polycrystalline nature and higher defects density of the former. Molecular doping of graphene via electron transfer increases the carrier density while leaving the dopant ions on the surface, which can act as charged impurities that increase the scattering of carriers and hence reduce the mobility as shown in Figure 4d. The Hall mobility decreases moderately for doped samples, but, for most of the dopants, is more
than compensated for by a larger increase of carrier density, which explains the net increase of the conductivity ($\sigma = e n \mu$) and measured decrease of the sheet resistance. The moderate reduction of the mobility in doped FLG in this work (24% and 17% for the strongest p- and n-dopants, respectively) can be contrasted to the larger reductions of mobility in doped SLG (26–80%) as summarized in Table S5. This difference can be attributed to the fact that charged impurities can be screened by each additional graphene layer, so that Coulomb scattering of the charged dopant ions on the surface of FLG doesn’t significantly affect the mobility of the buried layers of FLG. The smaller decrease in mobility for FLG on doping, therefore, less significantly offsets the accompanying increase in carrier density than in SLG. Importantly these results indicate that the transport properties of FLG are more robust to doping and work function modification than those of SLG.

Surface coverage estimates from XPS are in reasonable agreement with the order of magnitude of the calculated carrier densities from Hall measurements, and are similar to those observed for SLG by Paniagua et al. For example, Mo(tfd-CO$_2$Me)$_3$, Mo(tfd-COCF$_3$)$_3$, and Magic Blue display coverages of $0.28 \times 10^{13}$, $0.73 \times 10^{13}$ and $10 \times 10^{13}$ Dopants/cm$^2$ after 60 minutes, which are roughly comparable to the increases in carrier density. Discrepancies can arise due to some of the dopant species being physisorbed as neutral species rather than undergoing electron transfer (although, as discussed above, this is not significant in the case of Magic Blue) and/or to some of the dopants reacting with impurities or defects on the surface, or with portions of the graphene that are electrically isolated from the bulk by defects, and, therefore, not generating carriers detectable in the Hall effect measurements. An example of the former effect is presumably occurring with the weakest p-dopant, Mo(PhBz-dt)$_3$, which demonstrates higher coverage but a very low contribution to the carrier density. The n-dopants also display a much lower carrier contribution relative to their surface coverage, which could be due to oxidation from air exposure just prior to the Hall effect measurement.
The extremely high coverage of \((\text{RhCp}^*\text{Cp})_2\) does assist in explaining the drop in mobility of this sample, if the oxidized dopants are indeed acting as scattering sites.

### 2.5. Effect of doping time on the transport properties of solution-doped few-layer graphene

Aiming to determine the optimum dopant amount to yield the best performance of FLG as a TCE, we have varied the dipping time of samples in the dopant solutions and then characterized the transport properties and surface morphology. In **Figure 5a**, we plot the sheet resistance with respect to solution-dipping time for all p-dopants. Dipping the samples for 10 min (mild exposure) generally yields no significant reduction in the sheet resistance compared to the pristine sample with the exception of Magic Blue, the strongest p-dopant. The sheet resistance dips to a minimum at the 60 min mark, after which it rises steadily for all dopants. This trend can be understood by measuring the variations in the carrier density and Hall mobility, plotted in **Figure 5b** and **5c**, respectively. The data show a poor doping level initially for mild exposure time (10 min) which, increases with dipping time up to 60 min. Longer exposure to the dopant solution reduces the carrier density indicated by the Hall effect measurements and increases the mobility, suggesting less efficient generation of free carriers. This will be discussed in the next section.

To gain insight into the dominant scattering mechanism in molecular-doped FLG, we have plotted the mobility as a function of carrier concentration for p-dopants (**Figure 5d**). The observation of a universal negative correlation for all dopants suggests that charged impurity scattering (i.e., scattering by the charged dopant ions present on the surface) is the main scattering mechanism. However, the role of defects and phonon scattering cannot be completely excluded, since heavily p- and n-doped graphene could be reactive to nucleophiles and electrophiles respectively, and potentially such species could be present in solvent as trace impurities or even in glove-box atmosphere.
2.6. Effect of doping on the surface morphology of few-layer graphene

We examine the surface morphology of doped FLG via scanning tunneling microscopy (STM) and atomic force microscopy (AFM) (shown in Figure S5) for clues about the adsorption and aggregation behavior of molecular dopants for different solution-doping durations of 10, 60 and 180 min. In Figure 6, we show the STM topographic images of pristine FLG (Figure 6a) and FLG-doped with the Magic Blue p-dopant (Figure 6b-d). The dopant appears as bright spots on the surface of FLG as indicated by the red arrow in Figure 6b. At the lowest exposure time of 10 min (Figure 6b), we observe the formation of a disjointed molecular wire, presumably of SbCl$_6^-$ dopant ions or small clusters thereof, extended several tens of nanometers across the sample. Presumably like-charged dopant ions would not aggregate on a completely uniform graphene surface for Coulombic reasons and the aggregation here may be driven by inhomogeneities (e.g. grain boundaries) in the underlying electrostatic landscape of the FLG. Increasing the solution-doping time to the optimum 60 min duration results in a uniform distribution of nanoclusters and nanowires across the entire sample surface (Figure 6c). At the extended solution-doping time (180 min), the surface appears to be covered with molecules as we no longer see the isolated bright spots, indicating nearly full coverage of the FLG surface. Visually, these images correspond well to calculated monolayer coverage (assuming hexagonal close-packing of SbCl$_6$ ions) of ca. 25, 47, and 81% of a monolayer for the 10, 60, and 180 minutes immersed samples respectively, keeping in mind that these values may not indicate a continuous monolayer (i.e. clusters and bare patches may exist) and that well-dispersed single dopant molecules might not be observable by STM. Topographic line scans (Figure 6e) confirm the surface features become increasingly taller and coarser, as an indication of clustering of the dopant ions over time. This is further supported by the statistical distribution of apparent surface height shown in
Figure 6f, which exhibits an increase in the mean apparent height and the width of the distribution.

3. Discussion
Theoretical and experimental studies have identified Coulomb impurity scattering as the dominant scattering mechanism in graphene, rather than other common scattering mechanisms, such as short-range (defect) and phonon scattering. In pristine graphene, random impurities providing both negative and positive charges coexisting on the surface of graphene and in the underlying substrate are believed to generate electron-hole puddles that form the main scattering mechanism. Due to the presence of the electron-hole puddles in pristine graphene, the initial stage of doping has been reported to act as a neutralizing stage for such impurities, which results in no increase in the carrier density in graphene. In addition, the mobility either increases or minimally decreases in that regime, contrary to what is expected for the charge-impurity scattering mechanism explained above. This regime resembles the behavior of solution-doped FLG for the shortest dipping time (10 min). Here, dipping the FLG in the dopant solutions (toluene and DCM) inside the glovebox is likely to further clean the surface from PMMA residues and environmental contaminants, hence leading to a more intrinsic pristine FLG mostly by eliminating the p-type characteristic of FLG ascribed to its preparation and transfer, rather than to molecular doping alone (see SI for more information). Indeed, the p-doping resulted in no increase in the carrier density in FLG and the measured mobility was either unchanged or slightly higher than pristine graphene, depending on the dopant used. An apparent exception to this behavior was that of Magic Blue, which has the highest redox potential and can presumably also dope the FLG in a shorter time scale due to its higher doping strength. The initial increase in mobility reported for some molecular dopants has been observed before and was theorized to result from a
compensation effect of the random charged impurities between the graphene and the substrate where the molecules push such impurities farther from the graphene surface.\textsuperscript{[77]}

Upon increasing the dipping time to 60 min, the induced charge-carrier density increases in accordance to dopant strength, while the mobility drops due to charge-impurity scattering as discussed earlier. This regime presents the optimum condition for FLG doping, as the reduction in mobility is compensated by the larger increase in the carrier concentration and hence yields the lowest sheet resistance values.

Further increasing the doping time (180 min), reverses the positive trend in conductivity: the carrier concentration decreases while the mobility increases and was recently reported to universally occur for various dopants on graphene.\textsuperscript{[72]} Increasing the concentration of dopants can either cause more clustering of dopants\textsuperscript{[79]} – as we have observed in Figure 6b and 6c – or change their orientation and can even promote the layer-by-layer growth of multilayered structures, which we suspect is occurring in Figure 6d.\textsuperscript{[80]} Layering of the dopant may decrease the likelihood of forming additional charged impurity scattering centers and may in fact decrease the scattering as compared to FLG doped for 60 min as the dopants would lie farther from the graphene surface due to dopant-dopant interactions, which would explain the increase in mobility at this stage. Surprisingly, the transport measurements (Figure 5) show a decrease in carrier densities at higher dipping times despite a higher surface coverage of dopant species. While previous studies have found that longer exposure times can result in a lower doping efficiency, i.e., a lower % of the dopants present undergoing electron transfer, the absolute number of carriers still increases.\textsuperscript{[41]} Moreover, at least in the case of Magic Blue, XPS analysis indicates the presence of increased levels of Sb and Cl on the surface (and the absence of Br and N), suggesting more SbCl\textsubscript{6}\textsuperscript{−} is present and, therefore, that more holes are introduced at longer exposure times. The work function continues to shift as well with increased dipping time, an effect which is more prominent in the case of Magic Blue (Figure 2d). It is believed that the vacuum level shift contribution due to dipole formation may
dominate at this stage, since the shift in the Fermi level, as deduced from the shifts in the XPS C1s peak, appear to be negligible between doping times of 60 and 180 min for most dopants as shown in Figure S1a. Note that this is generally expected, since the relative importance of vacuum level shift vs. band filling / emptying increases with dopant coverage, as the former is proportional to the number of dopants that react whereas the latter is a function of the square root of the number of dopants that react. The explanation for this behavior is not clear at the present stage, but the data imply that at higher exposure times, a large portion of the carriers expected to be generated by the dopant are not able to contribute to the Hall current. These results reveal that while molecular doping can be effective in its current form, challenges remain to understand the effects of long exposure time and of high dopant coverage and to obtain further improvement in the FoM.

4. Conclusion
We have demonstrated the effect of molecular doping on FLG using solution-processed and stable metal-organic n- and p-dopants exhibiting a wide range of doping strengths as measured by their redox potentials, compared approximately to the potential of electrons at the Fermi level of pristine FLG. The effect of dopants on the work function, sheet resistance, carrier density and Hall mobility was presented and generally showed a direct correlation with the dopant strength. The wide tunability range of the work function of doped FLG combined with minor reductions in the carrier mobility as compared with SLG, where there is no screening of Coulomb scattering from the charged dopants, allows for the opportunity to produce FLG layers with high mobility and broadly tunable workfunction for utilization in electrode applications and beyond. Doping is shown to occur via electron transfer between FLG and the dopants, leaving the latter as a charged ion (charged impurity) on the surface.
This is shown to have a neutralizing effect on the substrate-induced impurities at low dopant concentration leading to a slight change of the mobility, which even increased in some cases. At moderate doping levels, the dopant species on the FLG surface lead to charge-impurity scattering and consequently to a decreased mobility. However, due to the large induced carrier density, the sheet resistance is minimized at this stage and the FoM of FLG increases in all instances. With prolonged exposure, the sheet resistance increases and the number of free carriers in the FLG decreases in apparent contradiction to what can be inferred from XPS and UPS, presumably suggesting that a large proportion of the contributed carriers are immobile. The sheet resistance values presented for doped FLG are suitable for touch screen applications which typically require values < 500 Ω/□. However, our finding of markedly different behavior in different doping regimes emphasizes the necessity of experimental methods of controlling the amount of molecular doping in FLG, which can play an important role towards enhancing the FoM for utilization of FLG as a TCE in optoelectronic and photovoltaic applications.

5. Experimental Section

*Source of dopants:* (RhCp*Cp)$_2$,$^{[54]}$ (RuCp*mes)$_2$,$^{[52]}$ Mo(tfd-CO$_2$Me)$_3$,$^{[47]}$ and Mo(tfd-COCF$_3$)$_3$$^{[41]}$ were synthesized as previously described. Magic Blue was obtained from Aldrich. The new compound Mo(PhBz-dt)$_3$ was synthesized as described below. Redox potentials of the molybdenum complexes were determined by differential pulse voltammetry in dichloromethane / 0.1 M Bu$_4$NPF$_6$ using a BAS potentiostat, a glassy carbon working electrode, a platinum auxillary electrode, a AgCl-coated Ag wire as a pseudo-reference electrode, and ferrocene or cobaltocenium hexafluorophosphate to internally reference the voltammograms to the ferrocenium/ferrocene couple (E(FeCp$_2$$^{2+/0}$) = −1.32 V vs. FeCp$_2$$^{2+/0}$).$^{[81]}$ The redox potential for Magic Blue was taken from ref [48]. The effective redox potentials for the organometallic dimers were estimated from Eq. 1 using the peak potentials for reduction
of the corresponding monomer cations obtained by cyclic voltammetry in THF / 0.1 M Bu₄NPF₆ using ferrocene as an internal reference (scan rate = 50 mV s⁻¹, hardware as for Mo complexes) and values of ΔG_{Diss} obtained from DFT calculations as described in ref [52].

*Molybdenum tris(1-phenyl-2-benzoyl-1,2-dithiolene)*, Mo(PhBz-dt)₃. 1,3-Diphenylprop-2-yn-1-one[82] (1.3 g, 6.3 mmol) was added by syringe to a deoxygenated suspension of (NEt₄)₂MoS₉²⁻[83] (1.0 g, 1.55 mmol) in acetonitrile (10.0 mL) at room temperature under nitrogen. After 5 min at room temperature the reaction mixture was stirred at 50 °C for 23 h. After allowing to cool to room temperature, the reaction solution was filtered through Celite and the volatiles were removed under reduced pressure. The dark blue solid remaining was dissolved in dichloromethane and then methanol was added. The dichloromethane was removed under reduced pressure and the remaining methanol solution was cooled at −80 °C overnight. A copper-colored solid was collected by filtration, washed with methanol, and dried to give impure (NEt₄)₂Mo(PhBz-dt)₃²⁻ (1.2 g). ¹H NMR (400 MHz, acetonitrile-δ₃): δ 7.86 (m, 3H), 7.72 (m, 3H), 7.54–7.14 (m, 24H), 3.10 (q, J = 7.2 Hz, 16H, NCH₂), 1.14 (tt, J_H-H = 7.2 Hz, J_N-H = 2.0 Hz, 24H, CH₃).

To a solution of crude (NEt₄)₂Mo(PhBz-dt)₃²⁻ (1.0 g, 0.85 mmol) in CH₂Cl₂ (30 mL) an excess of NOPF₆ (0.70 g, 4.0 mmol) was added at room temperature under nitrogen. The reaction was stirred under nitrogen at room temperature for 6 h and was monitored by UV-vis. spectroscopy. The color of the solution turned from red-brown to green to blue, and brown gas was evolved. The reaction mixture was then filtered to remove insoluble impurities and dichloromethane was removed under reduced pressure to give a dark green solid, which was extracted with toluene (200 mL). This solution was concentrated under reduced pressure (to 25 mL) and hexanes (25 mL) was added; the solution was cooled at −80 °C overnight and the resulting green solid was collected by filtration, washed with hexanes. After drying, ca, 0.5 g of an impure product was obtained; this was purified by column chromatography (silica gel, dichloromethane / hexanes (3:2) as eluent) and recrystallization from dichloromethane /
hexanes to give a green solid (0.25 g, 22% overall from (NEt$_4^+$)$_2$MoS$_9^{2-}$). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.65 (d, $J = 7.6$ Hz, 6H), 7.52 (t, $J = 7.6$ Hz, 3H), 7.44 (d, $J = 7.6$ Hz, 6H), 7.36 (t, $J = 8.0$ Hz, 6H), 7.27 (m, 9H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$): $\delta$ 193.84, 179.04, 171.61, 139.22, 135.82, 133.84, 130.19, 129.52, 129.13, 128.41, 128.25. Anal. calcd for C$_{45}$H$_{30}$MoO$_3$S$_6$: C 59.59, H 3.33, S 21.21. Found: C 59.51, H 3.51, S 20.91.

Sample preparation and doping: Few layer graphene (FLG) -4 to 10 layers- grown by CVD on 300 nm Ni film on SiO$_2$/Si substrate were purchased from Graphene Supermarket. Graphene was transferred to 1×1 cm glass substrates using the conventional PMMA stamp-transfer method$^{[30]}$ followed by annealing in vacuum for 90 min at 450 ºC under argon and hydrogen gas flow. Solutions of 0.1 mg/mL of all dopants were prepared inside a nitrogen glove box with less than 0.1 ppm oxygen and moisture. Toluene was used as a solvent for all dopants, except for Magic Blue, for which dichloromethane was used due to its insolubility in toluene. FLG samples on glass were dipped in dopant solutions inside the glove box. Dopant uptake was controlled by increasing the dipping time. All samples were rinsed with the appropriate solvent after dipping to remove loosely bound molecules from the surface of the graphene.

Characterization: Photoelectron spectroscopy (UPS and XPS) was performed using an Omicron Nanotechnology (Taunusstein, Germany) UHV system at the Amassian lab in KAUST. XPS was measured with a monochromatic Al K$\alpha$ source (1486.7 eV), while a 1/12 attenuated He(I) excitation (21.22 eV) was used for UPS. A hemispherical energy analyzer EIS-Sphera was used to collect the spectra with pass energy of 3 eV and 20 eV for UPS and XPS respectively. A base pressure of about 4.0 × 10$^{-10}$ mbar was maintained throughout all measurements. The spectroscopic data were processed using CasaXPS (Casa Software Ltd) and Origin software. Scanning tunneling microscopy (STM) imaging was performed in ultrahigh vacuum conditions (5.0 × 10$^{-10}$ mbar) in a variable temperature STM (VT-STM; Omicron Nanotechnology). Graphene samples were kept at room temperature during
measurements. A chemically etched polycrystalline tungsten STM tip was used for imaging, which was further cleaned by electron bombardment in situ in UHV to reach atomically resolved imaging of HOPG. FLG samples on sputtered Ni on SiO$_2$/Si were mounted on a sample plate for STM studies. All images were acquired with a sample bias of $V_b = 0.6$ V and a tunneling current of $I_t = 0.3$ nA.

Raman Spectra were obtained using a LabRAM ARAMIS (Horiba Jobin Yvon, Inc) instrument using a 473 nm laser excitation, focused with a 100x objective with a spot size of $1 \mu$m and 0.5 mW power. The scattered signal was dispersed with using 1800 mm$^{-1}$ grating. The spectra ranging from 1200 to 2900 cm$^{-1}$ were collected in backscattering geometry.

A hand held 4-point probe (Jandel Engineering Ltd.) was used to measure the sheet resistance of the samples inside the glove box.

Room-temperature Hall effect measurements were performed using the van der Pauw method in a commercial Lakeshore 7700 system with reversible sweep of magnetic fields up to 20 kG using a 100 $\mu$A excitation current. Contacts were fabricated using conductive silver paste to fix low strain Ag alloy wires (Lake Shore PN 671-260) which were soldered to the sample holder. Calculations of carrier density and Hall mobility are explained in details in the supplementary information.

Optical transmittance measurements were performed using a F20-UVX spectrometer (Filmetrics, Inc.) equipped with tungsten halogen and deuterium light sources over the range from 400 nm to 700 nm.

**Supporting Information**
Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**
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Figure 1. The chemical structures of dopants used in this work and their redox potential vs. the ferrocenium/ferrocene couple. The strength of the dopants is defined by the separation of these levels from the $E_F$ of graphene in either direction. The FLG value represents the effective potential of pristine graphene is based on $-\Phi/e$, where $\Phi$ is the work function determined by UPS, allowing for the uncertainty in the absolute value of the ferrocenium / ferrocene vs. vacuum (−4.8 to −5.2 eV).
Figure 2. Photoelectron spectroscopy on doped FLG. (a) UPS secondary electron cut-off (SEC) of pristine FLG and doped FLG with various n- and p-dopants. (b) XPS C 1s peak for pristine FLG and p-doped FLG. (c) Work function deduced from UPS data in (a) \([\Phi = 21.22\text{-SEC}]\) for pristine FLG and doped FLG for 60 minutes. (d) Comparison of the work function of p-doped FLG treated for 60 and 180 minutes.
Figure 3. (a) Raman spectra of pristine and doped FLG showing the evolution of G-peak (left) and 2D-peak (right) of various p-dopants for 60 minutes dipping time. (b) G-peak position of FLG p-doped for 60 minutes and (c) 2D\textsuperscript{L} peak position of FLG p-doped for 60 minutes.
Figure 4. Transport properties of pristine FLG and doped FLG for 60 minutes dipping time. (a) Sheet resistance, (b) FoM of pristine sample (black), p-doped FLG (red) and n-doped FLG (blue) (c) carrier density and (d) Hall mobility for pristine FLG, n-doped FLG (blue shaded) and p-doped FLG (red shaded).
Figure 5. Effect of doping time on the transport properties of FLG. (a) Variation in Sheet resistance, (b) carrier density and (c) Hall mobility for p-doped FLG with various doping time (10, 60 and 180 minutes). The light blue dashed line represents the corresponding value of the pristine FLG sample for comparison. (d) Mobility vs. Carriers density of p-doped FLG.
Figure 6. STM images ($V_b = 0.6$ V $I_t = 0.3$ nA) of (a) pristine and p-doped FLG with Magic Blue for (b) 10 min with the red arrow pointing to dopants, (c) 60 min, (d) 180 min and (e) line profiles along for pristine FLG and Magic Blue-doped FLG for 10 min and 60 min along the green lines shown in a, b and c (f) corresponding height distributions of pristine FLG and Magic Blue-doped FLG for various exposure times.
Solution-based non-covalent doping of few-layer graphene using novel metal-organic and organic molecules is demonstrated to enhance the conductivity and modulate the work function over a range of 2.4 eV with marginal reduction of mobility. The effects of dopant strength and coverage are shown to play crucial role in the optimization of the performance of few-layer graphene as a transparent conductive electrode.

Keyword: few-layer graphene, metal-organic molecular dopants, doping, transparent conducting electrodes, solution-processed


Facile doping and work-function modification of few-layer graphene using molecular oxidants and reductants

ToC figure
Supporting Information

Facile doping and work-function modification of few-layer graphene using molecular oxidants and reductants

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1. X-ray photoelectron spectroscopy and calculation of dopant surface coverage

Figure S1: (a) The binding energy of the fitted sp2 component in the C 1s XPS peak for p-doped FLG. (b) High resolution Cl 2p XPS peak for Magic Blue doped FLG for 10, 60 and 180 min dipping durations. (c) High resolution F 1s peak from Mo(tfd-COCF3)3 doped FLG for 60 and 180 min dipping durations. (d) High resolution F 1s peak from Mo(tfd-CO2Me)3 doped FLG for 60 and 180 min dipping durations.

The XPS area intensities were converted into relative atomic intensities after correcting for the relative sensitivity factors (RSF). First the C 1s intensity was adjusted to remove contributions from dopants using:
where \( I_{\text{Graphene}}^{\text{C}1s} \) is the relative atomic intensity of a core level orbital belonging exclusively to the dopant molecule such as F 1s, Mo 3d, Ru 3p, or Rh 3d, \( C_{\text{Dopant}} \) is the number of carbon atoms in the dopant and \( M_{\text{Dopant}} \) is the number of atoms of the exclusive element found in the dopant. Note that in the case of the ionic dopant Magic Blue, the carbon-containing moiety tris(4-bromophenyl)ammoniumyl is assumed to have been neutralized and removed from the surface during the rinsing step (as evidenced by the absence of measurable Br or N core ionizations), so this adjustment is not required.

Next the effective thickness \( x \) of the FLG was estimated assuming a uniform FLG layer on the SiO\(_2\) substrate by integrating the expected signal decay functions \(^1\) based on the inelastic mean free path \( \lambda \) \(^2\)

\[
I = I_0 \times \exp \left( -\frac{t}{\lambda \cos \theta} \right)
\]

and equating to the observed Si 2p and C 1s intensities:

\[
\frac{I_{\text{Obs}}^{\text{Si}2p}}{I_{\text{Obs}}^{\text{C}1s}} = \rho \int_0^\infty e^{-t/\rho} \, dt
\]

Depth inside the sample in nm is given by \( t \), \( \theta \) is the detection angle relative to the normal of the surface, \( B \) is a term that approximates for the atomic density in the scattering material (using the values for organic materials from ref [2]), and \( \rho \) is the estimated density of an element in the given material. Solving for \( x \) which, as expected, was close to 3 nm for each sample, the average number of layers is obtained by dividing \( x \) by 0.335 nm.

Finally, to determine surface coverage we need to correct the C 1s relative atomic intensity for attenuation within the FLG layer, based on the effective thickness \( x \):
From here we can determine Dopant/C\textsubscript{Graphene} based on the number of elements in the dopant, Dopant/nm\textsuperscript{2} from the number of carbons in 1 nm\textsuperscript{2} of SLG (38.17) multiplied by x/0.335, and % Monolayer based on the numbers of dopants per nm\textsuperscript{2} and the estimated area per dopant for a close-packed monolayer. For the n-dopants and Mo-based p-dopants, the footprint of the dopant molecules were taken from previous literature.\cite{3} For the ionic dopant Magic Blue, the SbCl\textsubscript{6}\textsuperscript{–} ion is assumed to sit on a triangular face of chlorine atoms, allowing the approximation of a cylinder with a diameter of 0.736 nm, determined by typical Sb-Cl bond lengths for SbCl\textsubscript{6}\textsuperscript{–} ions and the Van der Waals radius of chlorine. Assuming optimal hexagonal close packing of cylinders, this gives a 0.469 nm\textsuperscript{2} footprint.

The effective thickness and dopant coverage for the doped FLG films are summarized in Table S#. The Dopants/nm\textsuperscript{2} can give an estimate, assuming effective doping (which is supported by the core Ru 3p binding energies for the case of (RuCp*mes)\textsubscript{2} and by the absence of N and Br ionizations for the case Magic Blue), of the expected contribution of charge carriers, and display values comparable with the values given in Figure 4. The excessive coverage of (RhCp*Cp)\textsubscript{2} can also account for the drop in mobility observed in that sample, possibly by increasing carrier scattering. Finally the values of Monolayer coverage seem to agree with the STM images of the Magic Blue-doped FLG. Note that these values are averages across the sample, and the distribution of surface dopants will not necessarily be homogeneous.

Table S1: Calculation of the dopants coverage for various dipping durations from XPS.

<table>
<thead>
<tr>
<th>Dopant Treatment</th>
<th>Effective Thickness (nm)</th>
<th># of Layers</th>
<th>Dopants/C\textsubscript{Graphene}</th>
<th>Dopants/nm\textsuperscript{2}</th>
<th>Monolayer (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magic Blue</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-10 minutes</td>
<td>3.54</td>
<td>10.6</td>
<td>0.00134</td>
<td>0.542</td>
<td>25.4</td>
</tr>
<tr>
<td>-60 minutes</td>
<td>3.43</td>
<td>10.2</td>
<td>0.00256</td>
<td>1.00</td>
<td>46.9</td>
</tr>
<tr>
<td>-180 minutes</td>
<td>3.50</td>
<td>10.4</td>
<td>0.00431</td>
<td>1.72</td>
<td>80.8</td>
</tr>
<tr>
<td>Mo(tfd-COCF\textsubscript{3})\textsubscript{3}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2. Hall effect measurements

Hall effect measurements were employed to characterize the transport properties of pristine and doped FLG to determine the carrier density and type. The van der Pauw technique that is typically considered as an inseparable part from any Hall measurements is used to calculate the sheet resistance samples. The measured Van der Pauw sheet resistance generally agrees with the values measured from the linear four-point probe measurements conducted in glove box as shown in Table S1.

Table S2: Comparison of sheet resistance values obtained for p-doped FLG obtained from linear four-point probe in glove box and Van der Pauw technique in air.

<table>
<thead>
<tr>
<th>Dopant treatment</th>
<th>10 minutes</th>
<th>60 minutes</th>
<th>180 minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4-pt probe</td>
<td>Van der Pauw</td>
<td>4-pt probe</td>
</tr>
<tr>
<td>Magic Blue</td>
<td>520 ± 44</td>
<td>583</td>
<td>403 ± 35</td>
</tr>
<tr>
<td>Mo(tfd-CO₂Me)_3</td>
<td>979 ± 15</td>
<td>940</td>
<td>626 ± 10</td>
</tr>
<tr>
<td>Mo(tfd-CO₂Me)_3</td>
<td>1069 ± 55</td>
<td>891</td>
<td>908 ± 17</td>
</tr>
<tr>
<td>Mo(PhBz-td)_3</td>
<td>1078 ± 33</td>
<td>1010</td>
<td>865 ± 23</td>
</tr>
</tbody>
</table>

The Hall mobility is typically obtained by combining the information obtained from measuring the Hall Effect, namely, sheet carriers’ concentration and type, and the sheet resistance obtained from the van der Pauw technique, according to the following equation:

$$\mu = \frac{|V_H|}{R_s \times I \times B} = \frac{1}{q \times n_e \times R_s}$$

Hall Effect measurement:
Where $\mu$ is the Hall mobility, $V_H$ is the Hall voltage, $R_s$ is the sheet resistance, $I$ is the excitation current, $B$ is the magnetic field, $q$ is the elementary charge ($1.602 \times 10^{-19}$ C), and $n_s$ is the sheet carrier concentration.

Table S3: The sheet Hall coefficient of pristine FLG and doped FLG for n- and p-dopant for various dipping times.

<table>
<thead>
<tr>
<th></th>
<th>Sheet Hall coefficient [cm²/C]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n-dopants</td>
</tr>
<tr>
<td>Pristine</td>
<td>(RuCp*mes)$_2$</td>
</tr>
<tr>
<td></td>
<td>Mo(PhBz-td)$_3$</td>
</tr>
<tr>
<td></td>
<td>Mo(tfd-COCF$_3$)$_3$</td>
</tr>
<tr>
<td>2.1 × 10⁵</td>
<td>-1.1 × 10⁵</td>
</tr>
<tr>
<td>10 min</td>
<td>2.4 × 10⁵</td>
</tr>
<tr>
<td>60 min</td>
<td>1.6 × 10⁵</td>
</tr>
<tr>
<td>180 min</td>
<td>1.9 × 10⁵</td>
</tr>
<tr>
<td></td>
<td>2.2 × 10⁵</td>
</tr>
</tbody>
</table>

3. Raman Spectroscopy

3.1 Fitting of the 2D peak

The shape of the 2D-peak is typically used to identify the number of layers in graphene, for which a single Lorentzian peak is characteristic of a monolayer, whereas it can be deconvoluted into a number of peaks depending on the number of layers and their stacking until it resembles the 2D peak of graphite (two Lorentzian peaks) when $n > 5$, with the higher energy peak is more intense, reflecting the evolution of the electronic structure. However, such identification is only valid for graphene layers stacked in an AB-Bernal order. For randomly stacked graphene layers (turbostratic) the 2D-peak has the same shape as that of monolayer graphene due to the resemblance of its electronic structure. The shape of the 2D-peak of FLG in this work can vary in shape over different regions on the sample due the patchy nature of FLG, and can be fitted well using two Lorentzian peaks, as shown in Figure S2. However, the higher energy component shows a lower intensity in contrast to AB-Bernal stacked graphite. A similar trend has been observed in epitaxial graphene grown on the carbon facet of SiC, and was interpreted as partially ordered stacked sheets. The variation in the
intensity and position of the lower energy peak with changing thickness is an indication of its higher sensitivity to the electronic structure evolution.

Figure S2: Raman 2D peak of pristine FLG and p-doped FLG for 60 min and the corresponding fitting peaks.

3.2 Analysis of Raman spectra parameters for p-doped FLG with varying exposure times

Figure S3: The variation of I(2D)/I(G) (top row), G-peak position (middle row) and G-peak FWHM (bottom row) for Pristine and p-doped FLG at 10 min (left column), 60 min (middle column) and 180 min (right column) dipping time.
4. Transmittance data

Figure S4: Transmittance spectra of pristine and doped FLG with n- and p-dopants for 60 min dipping time.

5. Atomic force microscopy

Figure S5: AFM images of p-doped FLG for 60 and 180 min dipping time for (a) Magic Blue, (b) Mo(tfd-COCF$_3$)$_3$, (c) Mo(tfd-CO$_2$Me)$_3$ and (d) Mo(PhBz-td)$_3$.

6. The effect of dipping FLG in toluene – control experiment

To gain insights on the initial regime of doping (10 min) where a weak doping effect was observed, we run a control experiment of dipping as-prepared FLG in toluene without dopants inside the glove box.
The sheet resistance was observed to increase after dipping in toluene as measured by both linear 4-point probe and Van der Pauw method in air. Hall Effect measurement shows that the sheet Hall coefficient increases and the carrier density decreases in an indication of a reduction of the majority free carriers in FLG (holes) after dipping as a result of further removal of PMMA residues and other contaminants. However, since the Hall effect measurements requires taking the samples out of the glove box and be exposed to air during the sample preparation (ca. 30 min of ambient exposure prior to measurement), the samples were still showing a p-type characteristic. The results are shown in Table S4.

Table S4: Transport properties of as-prepared FLG and FLG dipped in toluene inside the glove box for 10 minutes. Transport measurements were done in air.

<table>
<thead>
<tr>
<th>Sample treatment</th>
<th>Sheet Resistance (Ω/sq)</th>
<th>Sheet carrier density (1/cm²)</th>
<th>Sheet Hall coefficient (cm²/C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-prepared</td>
<td>897 ± 27</td>
<td>831</td>
<td>4.9 × 10¹³</td>
</tr>
<tr>
<td>Dipping in Toluene</td>
<td>1018 ± 29</td>
<td>863</td>
<td>3.65 × 10¹³</td>
</tr>
</tbody>
</table>

7. Comparison to the reduction in mobility in non-covalently doped SLG (literature)

Table S5: Reduction in mobility in non-covalently doped SLG presented as the ratio of the change of mobility upon doping Δμ to the mobility in pristine SLG μ₀ in each reference.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>type</th>
<th>Δμ/μ₀</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(tfd-COCF₃)₃</td>
<td>p</td>
<td>-61%</td>
<td>[3]</td>
</tr>
<tr>
<td>Pentaethylenehexamine (PEHA)</td>
<td>n</td>
<td>-48%</td>
<td>[7]</td>
</tr>
<tr>
<td>Poly(ethyleneimine) (PEI)</td>
<td>n</td>
<td>-62%</td>
<td>[7]</td>
</tr>
<tr>
<td>Triethylene tetramine (TETA)</td>
<td>n</td>
<td>-26%</td>
<td>[8]</td>
</tr>
<tr>
<td>Nitric Acid (HNO₃)</td>
<td>p</td>
<td>-78%</td>
<td>[9]</td>
</tr>
<tr>
<td>Hydrazine</td>
<td>n</td>
<td>-37%</td>
<td>[9]</td>
</tr>
<tr>
<td>Poly(ethyleneimine) (PEI)</td>
<td>n</td>
<td>-67%</td>
<td>[9]</td>
</tr>
<tr>
<td>Tetraacyanoethylene (TCNE)</td>
<td>p</td>
<td>-80%</td>
<td>[10]</td>
</tr>
<tr>
<td>Gold Chloride (AuCl₃)</td>
<td>p</td>
<td>-37%</td>
<td>[11]</td>
</tr>
<tr>
<td>NH₂-SAMs</td>
<td>n</td>
<td>-53%</td>
<td>[12]</td>
</tr>
<tr>
<td>Impurities on SiO₂ substrate</td>
<td>p</td>
<td>-64%</td>
<td>[12]</td>
</tr>
</tbody>
</table>

Supporting information References:


