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Aryl Migration on Graphene

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KEYWORDS dynamic covalent chemistry, graphene, biphenyl, aryl shift

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ABSTRACT: The design and synthesis of molecular systems able to carry out movements resembling macroscopic objects is an exciting and challenging endeavor. Molecules that can walk covalently on a track have been demonstrated and we now report how aryl groups that can migrate over a graphene surface. Specifically, we describe a system comprised of covalently functionalized aryl groups on graphene that undergo continuous aryl shifts. The dynamic aryl shift allows the aryl groups on graphene to effectively walk step-by-step wherein each step involves reversible bond breaking and making that is initiated by a combination of an activated arene and p-doping of the graphene surface. Raman spectroscopic mapping of the distribution of the covalent attachment revealed that activated 4-methoxyphenyl groups migrate several microns from regions of high functionalization to regions with no prior functionalization.

Movement is a fascinating and essential attribute shared by most life forms. Macroscopic organisms derive this property by a complexity of interactive systems that are at their most elemental level enabled by molecular processes. Molecular motor proteins cause movements to carry out essential biological functions and represent some of the most exquisite examples of nanoscopic systems found in nature.[1,2] Nature's successful translation of molecular processes into physical movement has inspired the design of synthetic molecular systems that mimic macroscopic machines or objects. In this context, there have been advances in chemical synthesis and nanoscience to control the dynamics and movement of artificial molecular architectures.[3–6] Elegantly designed molecular systems exhibiting movement include nanocars,[7,8] molecular shuttles,[9,10] molecular walkers,[11,12] and other systems.[3–6]

With the long-term goal of directing movement and the spontaneous creation or molecular-scale objects, we report herein on reversible chemical reactions that allow for functional groups to walk freely on a graphene surface. Our architectural design is inspired to the 1,2-migration of the phenyl group[13] in biphenyl[14,15] and had previously been observed in extended polycyclic aromatics.[16] ^{13}C-labeling studies in biphenyl ([1-^{13}C]biphenyl), showed that the phenyl group undergoes stepwise migration along the benzene ring. Scrambling of the isotopic label was observed at all positions of the benzene ring when [1-^{13}C]biphenyl was treated with acid (**Figure 1**).[14] Other detailed mechanistic studies on substituted arenes were shown to undergo aryl shifts via *ipso* arenium ion.[17,18] We recognized that aryl groups covalently attached to p-doped graphene have local structures isoelectronic to the presumed *ipso* arenium, and reason that aryl shifts can be facilitated by oxidation or treatment with acid (**Figure 1**). Furthermore, theoretical calculations reveal that the C–C bonds between graphene and the aryl groups are relatively weak as a result of the fact that the introduction of sp^3 carbons within the sp^2 network creates strain within the graphene sheet.[19] The combination of the structure similarities and

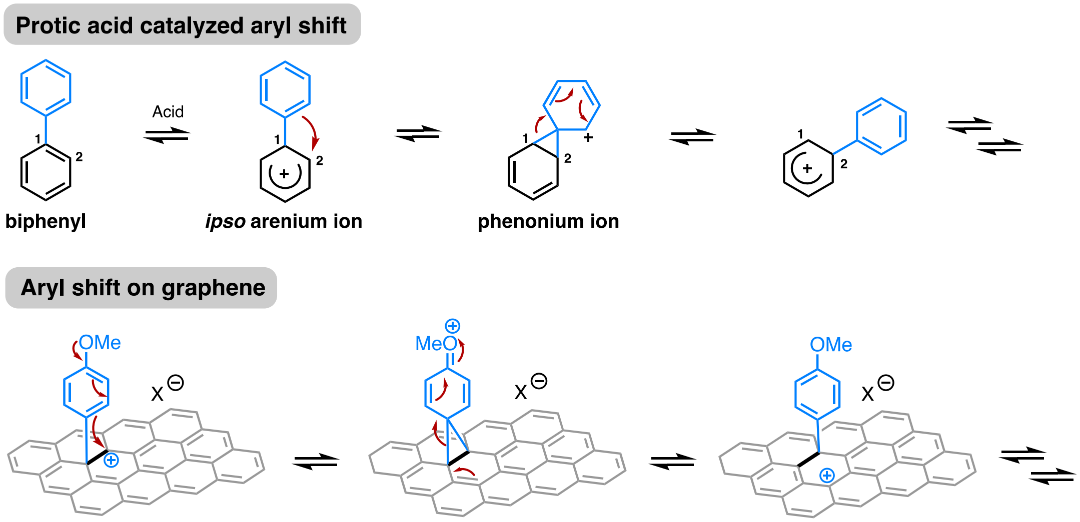

Figure 1. Aryl shift in biphenyl (top) and proposed aryl shift on graphene (bottom).

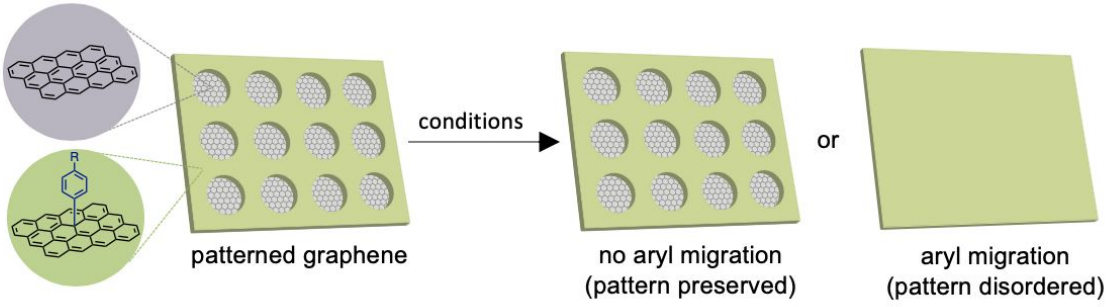

Figure 2. Schematic showing the characterization of aryl walking on graphene. If aryl shifts do not take place, the functionalization pattern on graphene remains the same (no aryl walking). If aryl shifts take place, the functionalization pattern on graphene becomes disordered or is completely lost (aryl walking).

weak bonds prompted us to explore aryl shifts on graphene surfaces. Although molecular mobility on surfaces has been previously demonstrated, these movements are primarily the result of sliding or rolling.[7,8,20] Small-molecule migrations along a track through covalent bond dissociation and bond formation have been demonstrated,[11,21] and we now present how aryl groups can migrate over large distances on the surface of graphene.

To determine the mobility of aryl groups on graphene we have experimentally examined the ability of aryl groups to redistribute on the surface. This approach is accomplished by patterning the graphene surface selectively with defined regions having arene functionalization and regions without arene functionalization (**Figure 2**). The aryl shift is then triggered by applying the appropriate conditions. As a result of the high strain in the high functionalization density regions and the drive to increase the system's entropy, the aryl groups migrate to blur the pattern and with high mobility eventually the functionalization becomes homogenous over microscales. Raman spectroscopy is established as the most important tool for characterizing graphene functionalization. The Raman spectrum of pristine or unfunctionalized graphene containing entirely of sp^2 carbons, displays two major bands: G (1850 cm^{-1}, a primary in-plane vibrational mode) and 2D (2690 cm^{-1}, a second-order overtone of the D band, another in-plane vibrational mode).[22] Covalent functionalization converts sp^2 carbons of graphene to centers with more sp^3 character at the site of attachment. These sp^3 carbons are recognized as defect sites on graphene and result in phonon scattering processes within the Brillouin zone of graphene.[23] This scattering causes the appearance of disorder peaks, including D (1350 cm^{-1}), D' (1620 cm^{-1}), and D+G (2940 cm^{-1}), in the Raman spectrum (**Figure S1**). The attachment of aryl groups involves covalent bond formation, and Raman spectroscopic mapping presents an ideal method for characterizing their distribution on graphene surfaces. Specifically, the intensity of the D band is indicative of the degree of functionalization, by examining the intensity ratio of the D and G peak, I_D/I_G, we can create a map of the location of aryl groups on the surface.[24]

We selected monolayer graphene (SLG) produced by chemical vapor deposition (CVD)[25] as a substrate for our study. Graphene produced by CVD are large continuous sheets with low defect density and can be transferred from the copper support onto other rigid flat surfaces. Depositing these large graphene sheet onto planar silicon wafers allow us to perform patterning processes by standard patterning methods. Given that the aryl groups must remain bound to the graphene at all times, they will not migrate over gaps in the graphene sheet, and as a result a continuous sheet is required. Although SLG, the thinnest two-dimensional material, cannot be clearly observed on all surfaces, it is readily observed under an optical microscope when deposited on silicon wafer that has 300 nm of SiO_2 layer. This advantageous feature allows us to carefully inspect the quality of the transferred graphene and determine that experiments are being performed on a continuous sheet.

Prior to patterning graphene, we applied our previously reported methods for the selective bulk covalent functionalization of carbon nanomaterials[26] on SLG on silicon wafer. These reactions are fast, efficient, and avoid the harsh reactivity associated with the more typical diazonium methods that can also produce dendritic arylene structures. Arene functionalization is achieved by reduction of SLG on silicon wafer in sodium naphthalide solution for 1 min followed by treatment with an iodonium salt solution at room temperature for 1 min. This method allowed us to selectively functionalize graphene with 4-trifluoromethylphenyl, phenyl, and 4-methoxyphenyl groups. Control experiments showed that the reaction requires reductive activation, similar to our previous studies on carbon nanotubes and graphite, to react with iodonium salts. As evident in the Raman spectra shown in **Figure 3a**, treating SLG with only sodium naphthalide or only bis(4-methoxyphenyl)iodonium tetrafluoroborate **1** did not enhance the disorder bands. The reaction is only successful when graphene is activated reductively, followed by reaction with iodonium salts as evidenced by the appearance of D, D' and D+G bands in the Raman spectra for 4-trifluoromethylphenyl, phenyl, and 4-methoxyphenyl functionalized graphene (SLG-$PhCF_3$, SLG-Ph, and SLG-PhOMe, respectively, **Figure 3a**). Successful functionalization was further confirmed by elemental analysis using X-ray photoelectron spectroscopy (XPS) and by infrared spectroscopy (IR). The F 1s peak at 688.7 eV was observed in the XPS spectrum of SLG-$PhCF_3$ (**Figure S2, S3**). The CF_3 stretch at 1337cm^{-1} in SLG-$PhCF_3$ and C–O stretch at 1261 cm^{-1} in SLG-PhOMe were observed in the IR spectra (**Figure S4**).

After confirming the selective functionalization of arenes on SLG, we proceeded with patterning. A scheme summarizing the steps in this process is shown in **Figure 3b**. A copper shadow mask containing patterned circular holes is fixed on top of SLG on silicon wafer. Copper is subsequently deposited on graphene and the mask is removed to reveal a layer of circularly patterned copper on graphene. The copper islands serve as a protective layer blocking graphene functionalization. Treating the copper patterned graphene with our aforementioned iodonium functionalization conditions selectively functionalizes the areas of graphene that are not covered by copper. Lastly, etching the copper islands on graphene produces SLG selectively patterned with arenes.

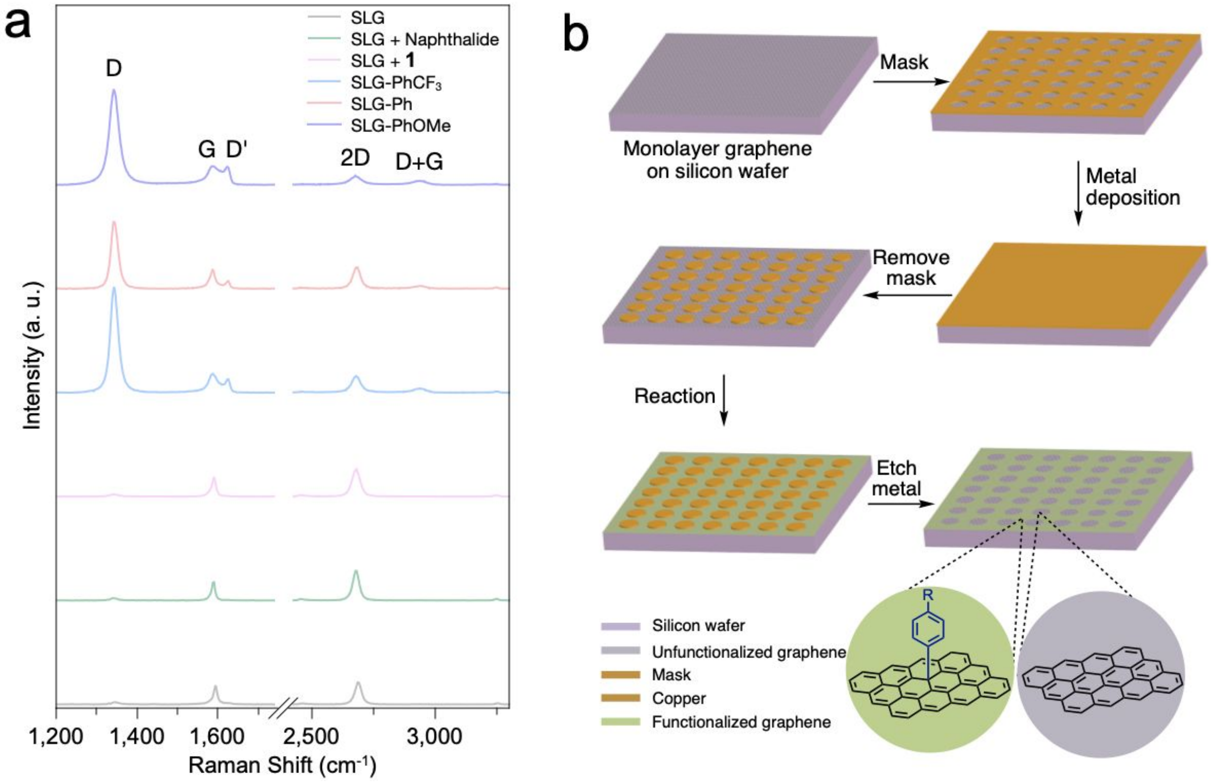

Figure 3. (a) Raman spectra of SLG, SLG treated with only sodium naphthalide, SLG treated with only iodonium salt, and SLG functionalized with 4-trifluoromethylphenyl, phenyl and 4-methoxyphenyl groups. (b) Graphene patterning process.

Graphene patterned with copper (**Figure S5a-b, S6a-b, S7a-b**) was functionalized with 4-trifluoromethylphenyl, phenyl, and 4-methoxyphenyl groups (**Figure S5c, S6c, S7c**). Analysis of the functionalized regions by Raman spectroscopy showed the characteristic appearance of the disorder bands, indicating covalent functionalization (**Figure S5d, S6d, S7d**). We also noticed a Raman peak appears in between the D and G bands of the functionalized graphene. This band is attributed to the formation of hydroxyl groups upon exposure of reduced graphene that has not been discharged from its n-doped state prior to quenching with water under ambient atmosphere.[27] We perform etching with ammonium persulfate[28] to oxidatively remove the copper islands and obtained the expected patterned graphene selectively functionalized with 4-trifluoromethylphenyl and phenyl groups according to plan (**Figure 4a-d, S5f-g, S6f-g**). In stark contrast, we do not observe a patterned surface for graphene functionalized with 4-methoxyphenyl groups (**Figure 4e-f, S7f-g**). The Raman map of the graphene has scrambled patterns, lacking the distinct circular patterns representing the original regions that were selectively functionalized and unfunctionalized. This observation is consistent with the oxidative etching triggering the migration of the 4-methoxyphenyl groups across the surface of the graphene.

We investigated substrate effects on graphene to further understand why the 4-methoxyphenyl migrates spontaneously with oxidative etching, whereas the 4-trifluoromethylphenyl and phenyl groups do not. Oxidative doping of graphene can be influenced by exposure to air and covalent functionalization. It has been shown that graphene on SiO_2 substrate possesses p-doping characteristics with air exposure or as a result of molecular oxygen trapped between graphene and the underlying substrate.[29] Covalent functionalization with aryl groups further increases the ease by which graphene can be p-doped.[30] The oxidizing copper etchant solution, consisting of ammonium persulfate in water,[31] as well as the dissolved copper ions, likely p-dopes graphene. Removal of electrons from graphene creates holes or positive charges on the surface activates graphene towards aryl shifts. In addition, the 4-methoxyphenyl group is highly activated and resonance structures of the presumed intermediate (**Figure 1 bottom**) are stabilized by the *para*-methoxy group.[32] As a result, it is reasonable that the combination of highly activated graphene surface and aryl group promotes the aryl shift in 4-methoxyphenyl functionalized graphene during the etch process. In contrast, the 4-trifluromethlphenyl group is electron-withdrawing and deactivating, and the unsubstituted phenyl group is insufficiently activated to afford migration. Control experiments confirmed that the etchant used to etch copper was not damaging the graphene and causing the observed increase in I_D/I_G across the graphene (**Figure S8**).

If we assume that an aryl group walks in the mechanism shown in **Figure 1** from the functionalized area along a straight path towards the center of a circularly unfunctionalized area with a radius of 3.25 µm, it requires approximately 26,530 steps. If the aryl groups walk at a rate similar to aryl shifts wherein the arenium rearrangement has free energy barriers of ~ 9–13 kcal/mol,[17] then we expect the aryl groups to travel between 13 to 11,392 µm in 1 min according to the Eyring equation and assuming a first-order reaction at 298 K. As a result, it is reasonable for the 4-methoxyphenyl to walk a distance of 3.25 µm. It is unlikely that the aryl groups migrate in a straight path. Instead, they are more likely take different paths influenced by encounters with other aryl groups along the path, as well as the structure and orientation of the different graphene domains that will likely affect the energy barriers. As a result, the disordered functionalization pattern demonstrates that aryl shifts on graphene are very dynamic and facile.

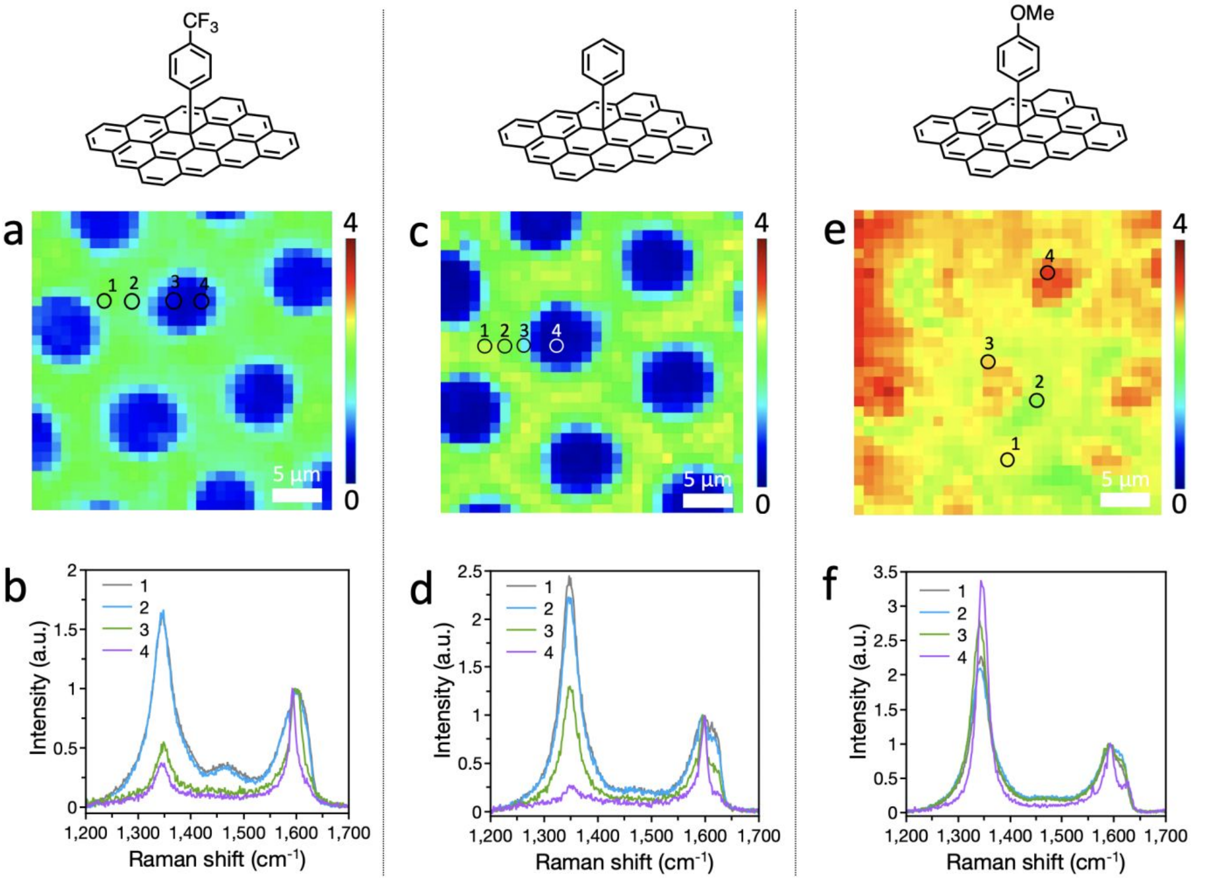

Figure 4. Raman I_D/I_G map of an area of functionalized graphene after copper etch (area of map is 30 µm x 30 µm). Functionalization patterns are readily distinguishable for graphene functionalized with 4-trifluoromethylphenyl (a) and phenyl groups (c). The functionalization pattern as revealed by Raman I_D/I_G map is lost for 4-methoxyphenyl functionalized graphene (d). (b, d, f) Raman spectra of the labeled areas in the corresponding Raman I_D/I_G map.

We have described here a system having aryl groups capable of diffusing on a two-dimensional graphene surface via dynamic covalent[33,34] aryl shifts. This system is comprised of 4-methoxyphenyl groups covalently attached to the graphene and we propose that the mechanism is similar to molecular processes previously reported. We believed the combination of a highly activated arene, 4-methoxyphenyl group, and p-type doping of graphene results the aryl shifts. Migration is confirmed by patterning graphene selectively with functionalized and unfunctionalized regions, and with oxidation the activated aryl groups walk from highly functionalized areas to unfunctionalized areas as revealed by Raman mapping. Future work will seek to better control the aryl migration on graphene surfaces to realize the potential of this process to create responsive nanoelectronics systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

General methods, graphene patterning, functionalization of graphene with iodonium salts, characteristic Raman bands of unfunctionalized and covalently functionalized graphene, XPS of unfunctionalized and 4-trifluoromethylphenyl functionalized graphene, FTIR spectra of functionalized graphene, Raman analysis of 4-trifluoromenthylphenyl, phenyl and 4-methoxyphenyl functionalized graphene, control experiment, Raman analysis of 4-methoxyphenyl functionalized graphene before and after walking, stability of methoxyphenyl group in ammonium persulfate solution, XPS analysis of 4-methoxyphenyl functionalized graphene, graphene transistor experiments (PDF)

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Author Contributions

All authors have given approval to the final version of the manuscript.

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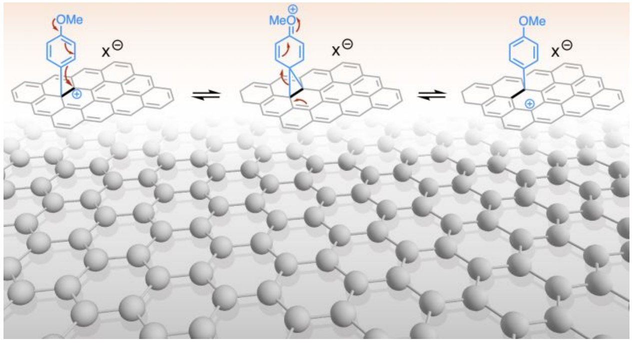
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