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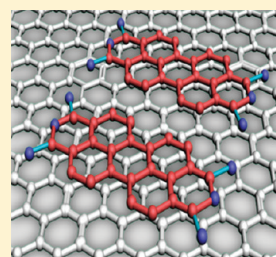
Tailoring Electronic Properties of Graphene by π – π Stacking with Aromatic Molecules

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ABSTRACT: Intrinsic graphene is a semimetal or zero bandgap semiconductor, which hinders its applications for nanoelectronics. To develop high-performance nanodevices with graphene, it is necessary to open the bandgap and precisely control the charge carrier type and density. In this perspective, we focus on tailoring the electronic properties of graphene by noncovalent stacking with aromatic molecules through π – π interaction. Different types of molecules (functioning as either an electron donor or acceptor when stacked with graphene) as reported in recent literature are presented regarding surface patterning, bandgap engineering, surface doping, as well as applications in nanodevices, particularly the field-effect transistors (FETs). On the basis of the current progress along this research line, future issues and challenges are also briefly discussed.



Graphene, a single atomic layer of sp^2 -hybridized carbon atoms with honeycomb structure, has been attracting great deal of research interest due to its variable applications. Several perspective articles have already highlighted the recent research progress of graphene, particularly from the point of view of physical chemistry.^{1–6} Distinct from these perspectives, we herein specifically focus on how to tailor the electronic properties of graphene through noncovalent π – π stacking with aromatic molecules, which is mainly determined by the π – π interaction in conjunction with electron donor–acceptor (charge transfer) interaction. Different types of molecules (functioning as either electron donor or acceptor) as reported in recent literature are presented regarding surface patterning, bandgap engineering, surface doping, as well as applications in nanodevices, particularly field-effect transistors (FETs).

Graphene possesses unique properties of high carrier mobility, long phase coherence length, high thermal conductivity, and strong mechanical behavior, which combined make it a promising material for future carbon-based nanoelectronics.^{7–12} However, the valence and conduction bands of intrinsic graphene intersect at the Dirac point in the corners of a hexagonal Brillouin zone, making graphene a semimetal or so-called zero bandgap semiconductor. This hinders the development of graphene for application in nanoelectronics. In order to approach high-performance electronic devices, it is essential to generate bandgap in graphene to enable its semiconducting behavior and precisely control the charge carrier type (p-type vs n-type) and density.

So far, several approaches have been attempted to tailor the electronic properties of graphene. Atomic doping (e.g., by boron or nitrogen) as employed in traditional semiconductors has proven to be able to open the bandgap and make p-type or n-type graphene.^{13–15} However, the doping is usually difficult to control and often introduces defects and thus destroys the band structure. Another way is to modify graphene by covalent

modification, where the absorbed molecules form chemical bonds to the graphene surface.^{14,16,17} This type of chemical modification can usually generate stable structures, and represents one of the most promising methods for increasing the solution processability for printable graphene electronics. However, the covalent bonding changes the graphene's carbon hybridization from sp^2 to sp^3 , often leading to unwanted alteration or even destruction of the basic electronic properties of graphene.

In order to approach high-performance electronic devices, it is essential to generate bandgap in graphene to enable its semiconducting behavior.

Alternatively, the electronic properties of graphene can be tuned by noncovalent modification. Under such conditions, the interaction between absorbates and graphene surface are dispersive, which can preserve the desired electronic properties of graphene by minimizing the damage to the carbon lattice. Due to the large specific surface area of graphene sheet, the electronic effect caused by this kind of surface modification could be significant, providing a simple, but effective way to tailor the bandgap structure of graphene. Moreover, in the past decades, aromatic molecules have often been employed to modify the electronic properties of carbon nanotubes (CNTs).^{18,19}

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The molecules interact with the sidewall of CNTs by means of the so-named π - π stacking, a kind of van der Waals force relating to their π -electron backbone system, to form a stable hybrid structure and improve their electronic properties. The π - π stacking modification has been demonstrated to do much to preserve the desired properties. Graphene surface has a similar graphitic structure to the sidewall of CNTs; however, graphene possesses a planar π -surface that is more conducive to cofacial π - π stacking. It is thus expected that the noncovalent π - π stacking will open a promising way to precisely tailor the electronic properties of graphene so as to be suited for future application in nanoelectronics.

Graphene surface has a similar graphitic structure to the sidewall of CNTs; however, graphene possesses a planar π -surface that is more conducive to cofacial π - π stacking.

Stacking Aromatic Molecules on a Graphene Surface. Aromatic molecules, such as tetrafluorotetracyanoquinodimethanes (F4-TCNQ), perylene-3,4,9,10-tetracarboxylic-3,4,9,10-diimide (PTCDI), and its precursor perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride (PTCDA), have been widely used in organic semiconductors, as these molecules are proven effective for intermolecular π - π stacking through self-assembly processing.^{20,21} Recently, these aromatic molecules have been investigated for π - π stacking assembly on a graphene surface, where significant change of the electronic properties of graphene was observed, accompanied by efficient interfacial charge transfer.^{22–24} These aromatic molecules can be assembled on a graphene surface by the physical vapor deposition (PVD) method in an ultrahigh vacuum (UHV) chamber.^{25,26} By this method, the surface coverage and layers of molecules can be controlled by the depositing time, the molecular pressure, and the state of the graphene surface including temperature, undulation, defects, and so on. The aromatic molecules can also be transferred on graphene surface by drop-casting the solutions or immersing graphene samples in the solutions. With either of methods, the surface coverage can be adjusted by the concentration, the contacting time, and the rinsing afterward. The strong π - π stacking between the graphene surface and the aromatic molecules usually makes the surface stacking quite stable against rinsing or other solution processing.

By using scanning tunneling microscopy (STM), several groups investigated self-assembled PTCDA molecules on a graphene surface.^{23,25,26} PTCDA is a planar molecule based on a perylene backbone with a conjugated shape-persistent π -electron system (as shown in Figure 1a), which is highly suited for stacking onto a graphene surface. Besides tailoring the electronic properties, PTCDA derivatives were found to play an important role in the deposition of uniform ultrathin Al_2O_3 film that could act as high- k dielectrics for future nanoelectronics.²⁷ By low-temperature STM, Lauffer et al. found that PTCDA molecules can self-assemble on a bilayer graphene surface with a nonplanar brick-wall structure at a high density.²³ Although this specific phase may not be stable under ambient

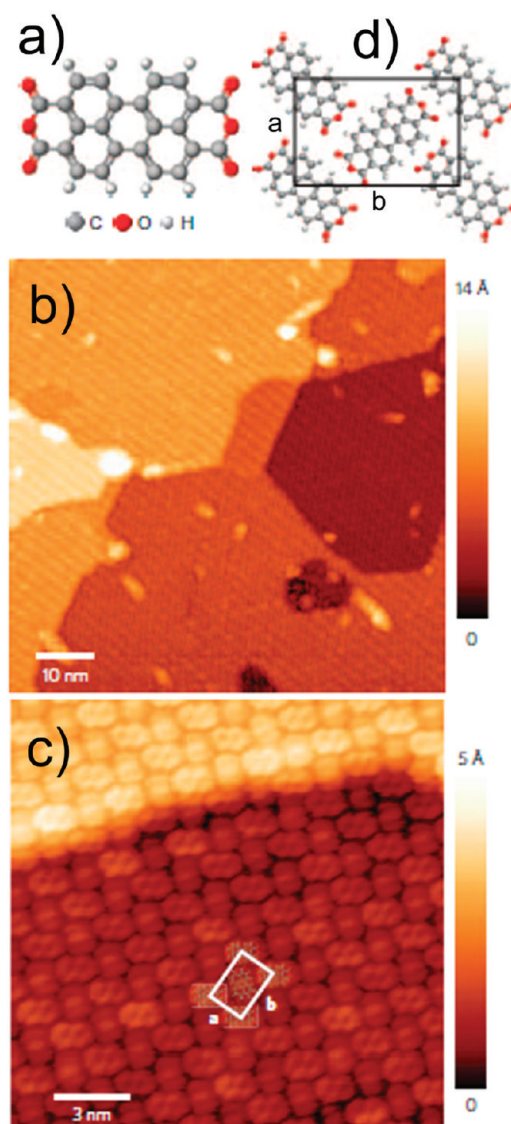


Figure 1. (a) Molecular structure of PTCDA. (b) STM image of the PTCDA monolayer assembled on a graphene surface. (c) Molecular-resolution STM image of the PTCDA monolayer. (d) Schematic herringbone unit cell of the PTCDA monolayer. (Adapted from ref 25 with permission. Copyright 2009, Macmillan Publishers Ltd.)

conditions, as they could only exist at 4.7 K, a stable, well-ordered, uniform monolayer of PTCDA molecules with herringbone structure was self-assembled on a graphene surface at 77 K or even room temperature.^{25,26}

Figure 1b,c show room-temperature STM images of monolayer PTCDA molecules self-assembled on a graphene surface. The PTCDA molecules are well-ordered with large domains over hundreds of nanometers. Figure 1c is a molecular-resolution STM image. A herringbone structure of PTCDA molecules was clearly observed, where PTCDA molecules lie flatly on the graphene surface with their π -planes parallel to the surface, exhibiting clear evidence that the PTCDA molecules are assembled on the graphene surface through π - π interaction. Furthermore, the herringbone monolayer of PTCDA molecules on graphene is stable even under laboratory ambient conditions.²⁵

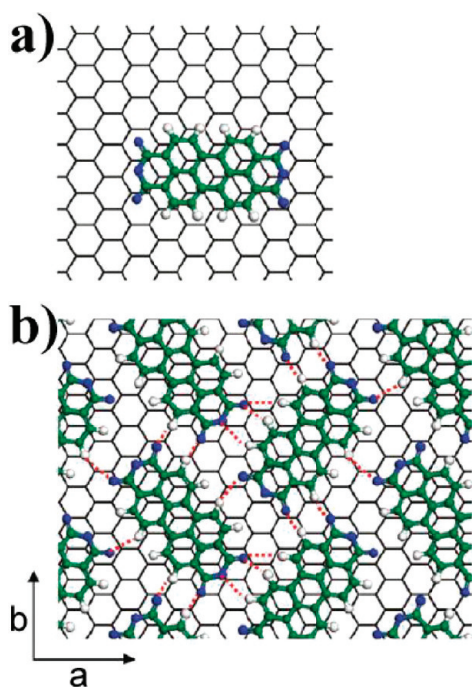


Figure 2. Calculated geometry configuration of PTCDA molecules on a graphene surface with (a) 1/3 monolayer and (b) 1 monolayer. (Adapted from ref 28.)

The noncovalent π – π stacking will open a promising way to precisely tailor the electronic properties of graphene so as to be suited for future application in nanoelectronics.

The assembly of PTCDA molecules as stacked on a graphene surface was also studied by density functional theory (DFT)-based *ab initio* calculation.²⁸ The results exhibit that a single PTCDA molecule is thermodynamically stable with the geometry configuration as shown in Figure 2a. In such a situation, the average distance between PTCDA molecules and the graphene surface is around 3.11 Å, and the absorption energy is 1.20 eV, which is the largest among other stacking configurations. Figure 2b shows an optimized structure of PTCDA molecules when forming a complete monolayer on a graphene surface. Here the PTCDA molecules form a herringbone structure, which is consistent with the experimental results obtained by STM imaging (Figure 1).^{25,26} These molecules are stabilized by two types of interactions, in-plane intermolecular interaction between the PTCDA molecules, and the PTCDA–graphene π – π interaction.

Bandgap Engineering. Some of the aromatic molecules such as PTCDI, 1,1'-azobis(cyanocyclohexane) (ACN), F4-TCNQ and 1,3,6,8-pyrenetetrasulfonic acid (TPA) can induce bandgap in graphene when they stack onto a graphene surface by π – π interaction.^{29–32} This noncovalent modification does not lead to

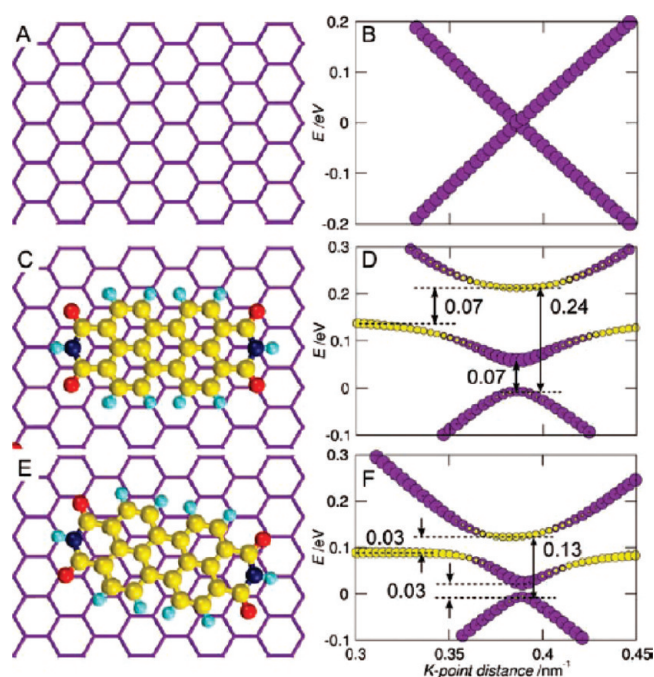


Figure 3. (a,b) Pristine graphene and the corresponding band structure. (c,e) Two types of PTCDI molecular configurations on a graphene surface. (d,f) Calculated band structures corresponding to panels c and e, respectively. (Adapted from ref 29 with permission. Copyright 2011, John Wiley and Sons, Inc.)

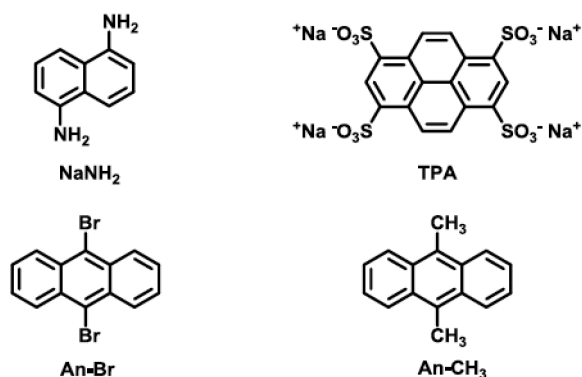
damage of the desired electronic properties of graphene, thus opening a simple way to engineer the bandgap of graphene.

On the basis of DFT calculations, it was found that stacking of a PTCDI molecule can open the bandgap of graphene by about a tenth of an electron volt.²⁹ The band structures of the graphene modified by PTCDI molecules are mainly relative to the graphene's valence bands (VBs) and conduction bands (CBs), and the lowest unoccupied molecular orbital (LUMO) of PTCDI. These bands interact near the Dirac point in different ways, resulting in opening of the graphene's bandgap. The effect of the stacked molecules on graphene band structures could be controlled by the stacked molecular configuration, the coverage of the active molecules, and the chemical modification of the active molecules. Figure 3 shows the calculated band structures of graphene without or with PTCDI molecules in different configurations. In Figure 3c, the PTCDI molecule has a similar configuration as that in Figure 2a. In this situation, the molecule is thermodynamically stable with the lowest energy among all configurations. Figure 3d is the corresponding calculated band structure. Direct bandgaps of about 70 and 240 meV were induced from the graphene VBs and PTCDI LUMO bands to graphene CBs. Near the Dirac point, the PTCDI LUMO bands and graphene CBs are mixed and can be considered as an avoided crossing of both bands. It can be seen that the generated bandgap here is about 70 meV.

PTCDI molecules with a rotated configuration are shown in Figure 3e, which could be formed on the current knowledge of surface science. The corresponding band structure is shown in Figure 3f, where the bandgap induced in graphene is about 30 meV, which is much smaller than that generated for the configuration of Figure 3c. This implies that the bandgap thus generated in graphene can be tailored by controlling the stacking configurations.

Table 1. PTCDI Molecules with Tunable HOMO and LUMO Levels^a

Molecule				
LUMO	-3.6 eV	-3.7 eV	-3.9 eV	-4.2 eV
HOMO	-6.1 eV	-6.3 eV	-6.4 eV	-6.7 eV

^a B3LYP/6-311g**//b3lyp/6-31g*, Gaussian 09 package.Scheme 1. Molecular Structures of Na-NH₂, TPA, An-Br and An-CH₃

The induced bandgap of graphene can also be tuned by the coverage of PTCDI molecules. The above-mentioned PTCDI molecular coverage on graphene surface is about 0.388 molecules/nm². Herringbone and brick-wall configuration are two typical structures observed for PTCDI molecules when stacked on a graphene surface at higher coverage of 0.677 and 0.595 molecules/nm², respectively. The herringbone structure leads to a bandgap of about 80 meV near the Dirac point, and the brick-wall structure leads to a bandgap of about 90 meV.²⁹ These calculated results confirm that the bandgap generated within graphene is somehow dependent on the surface coverage of active molecules.

Since the PTCDI LUMO band plays an important role in tuning the bandgap of graphene, one may attempt to gain the desired LUMO level by chemical modification of PTCDI molecules as shown in Table 1. The bay area of PTCDI is feasible for substitution with variable electron donor or acceptor moieties so as to shift the LUMO up or down. For the four molecules shown in Table 1, the LUMO can be tuned as large as 0.6 eV, while the bandgap remains almost unchanged around 2.5 eV. In the past decade, various PTCDI derivatives have been designed and synthesized in our lab, and the self π - π stacking interactions of these molecules have been extensively studied.^{20,33–40} The wide range of LUMO levels as attained for these modified PTCDI molecules will likely enable further adjustment of the bandgap of graphene. Moreover, the enhanced electron accepting capability of the cyano-substituted PTCDI is conducive to the *l*c p-type doping of graphene.

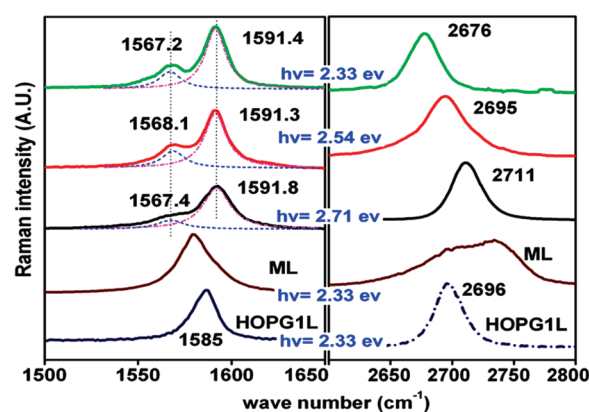


Figure 4. Raman G and 2D bands of a TPA-modified graphene monolayer excited by lasers with energies of 2.33, 2.54, and 2.71 eV, as well as a pristine multilayer (ML) and mechanically exfoliated HOPG monolayer (HOPG1L) excited by a laser of 2.33 eV energy. (Adapted from ref 30 with permission. Copyright 2009, American Physical Society.)

TPA (shown in Scheme 1) represents another typical aromatic molecule that has been employed for stacking with graphene and the bandgap modification. Figure 4 shows the Raman G-band spectra of graphene without and with TPA molecules stacked on the surface through π - π interaction. Exfoliated graphene shows a typical G-band around 1585 cm⁻¹. Upon stacking with TPA molecules, two obvious G-bands emerge at 1567 and 1591 cm⁻¹, exhibiting a clear G-band splitting compared to the pristine graphene. The splitting of the G-band means two phonon energies allowed at the Γ point. As indicated, it is ascribed to the graphene 6-fold symmetry breaking induced by the stacked TPA molecules. The symmetry breaking would result in modification of the electronic structure, i.e., bandgap could be induced within graphene with TPA molecules stacked on the face.³⁰ This is consistent with the calculations based on a tight-binding Hamiltonian model as performed for the same stacking of TPA molecules on the graphene surface.³¹

As a fundamental unit in integrated circuits, FETs remain a concentrated research area in nanotechnology, with the aim to miniaturize the device into nanoscale. Graphene now emerges as one of the most promising materials for development into FET nanodevices. Figure 5a schematically illustrates a typical bottom-gate FET fabricated with graphene. The conductivity of the graphene channel is controlled by the electric field in the dielectric induced by

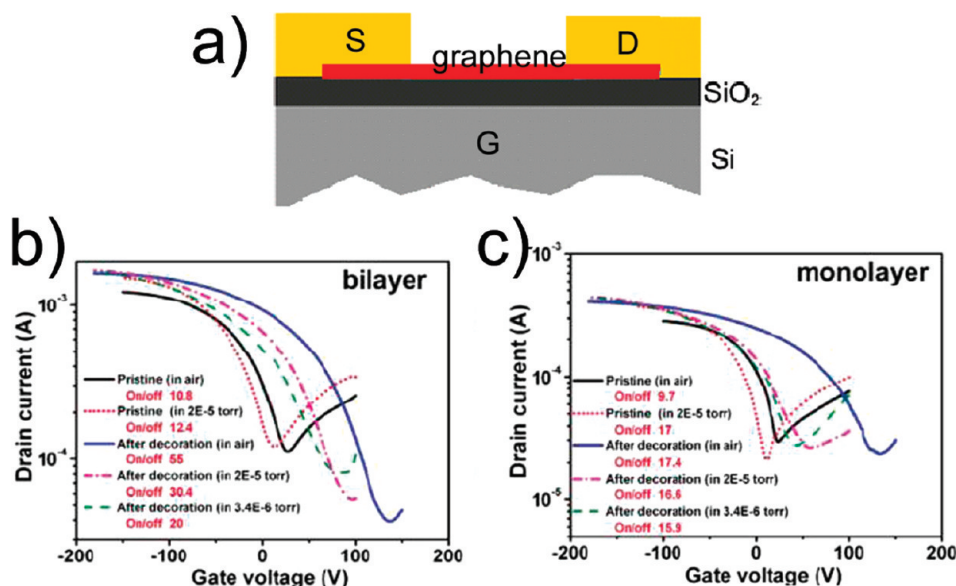
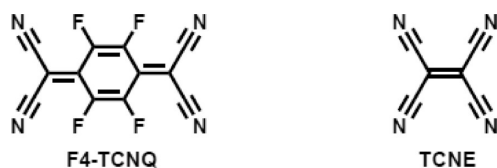


Figure 5. (a) Schematic illustration of bottom-gated graphene FET, where the SiO₂ serves as the dielectric, and doped Si serves as the gate electrode. (b) Transfer curves for bilayer graphene FET before and after triazine modification. (c) Transfer curves for monolayer graphene FET before and after triazine modification. (Adapted from reference 41.)

Scheme 2. The Molecular Structures of F4-TCNQ and TCNE



the gate voltage. Due to the zero bandgap, graphene-based FETs often show a low on/off ratio. The induced bandgap in graphene can improve the on/off ratio.⁴¹ As shown in Figure 5b,c, the on/off ratio of both the bilayer and monolayer graphene based FETs is significantly increased after surface modification with triazine, which causes the bandgap opening. In order to further improve the performance of graphene based FETs, more aromatic molecules with optimal π - π stacking with graphene will need to be studied so as to achieve larger bandgap opening and more effective charge separation.

Surface Doping. In order to develop graphene into high-performance carbon-based nanoelectronics, it is also critical to control the charge carrier type and density in the graphene sheet. Interfacial charge transfer often occurs between the stacked molecules and graphene when the LUMO and highest occupied molecular orbital (HOMO) of molecules match the VB and CB bands of graphene with sufficient driving force (ΔG).⁴² When the molecules function as an electron donor (i.e., electron transfer from molecules to graphene), n-type graphene will be produced, whereas p-type graphene will be generated when the stacked molecules act as an electron acceptor.

Some aromatic molecules, e.g., F4-TCNQ, tetracyanoethylene (TCNE) (both shown in Scheme 2), TPA (shown in Scheme 1), act as strong electron acceptors as they are modified with strong electron withdrawing moieties. Once stacking onto graphene, efficient electron transfer occurs from graphene to the molecules, resulting in the formation of p-type graphene.^{43,44}

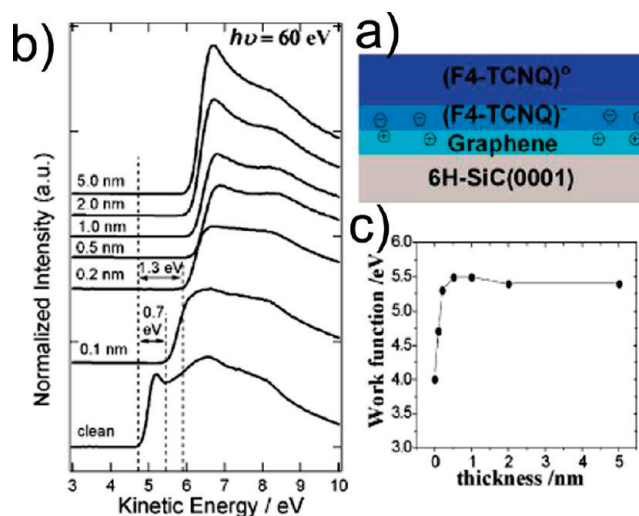


Figure 6. (a) Schematic illustration showing electron transfer from graphene to F4-TCNQ. (b) PES spectra at the low-kinetic energy region with different thicknesses of F4-TCNQ on the graphene surface. (c) The work function of graphene depending on the thickness of F4-TCNQ. (Adapted from ref 43.)

F4-TCNQ, as one of the strongest electron acceptors, has been widely studied for stacking onto graphene to produce p-doping, for which the interfacial charge separation (as shown in Figure 6a) is highly thermodynamically favorable due to the large driving force.

The charge transfer between graphene and F4-TCNQ can be characterized by high-resolution photoemission spectroscopy (PES).⁴³ Figure 6b shows the PES spectra at low-kinetic energy region of graphene covered with different thickness of F4-TCNQ. When covered with 0.1 nm thickness of F4-TCNQ layer, the work function of graphene increases 0.7 eV from 4.0 eV (for pristine graphene) to 4.7 eV. As shown in Figure 6b,c, the work function of graphene increases sharply with an increase in thickness of the F4-TCNQ layer, although it reaches a plateau after

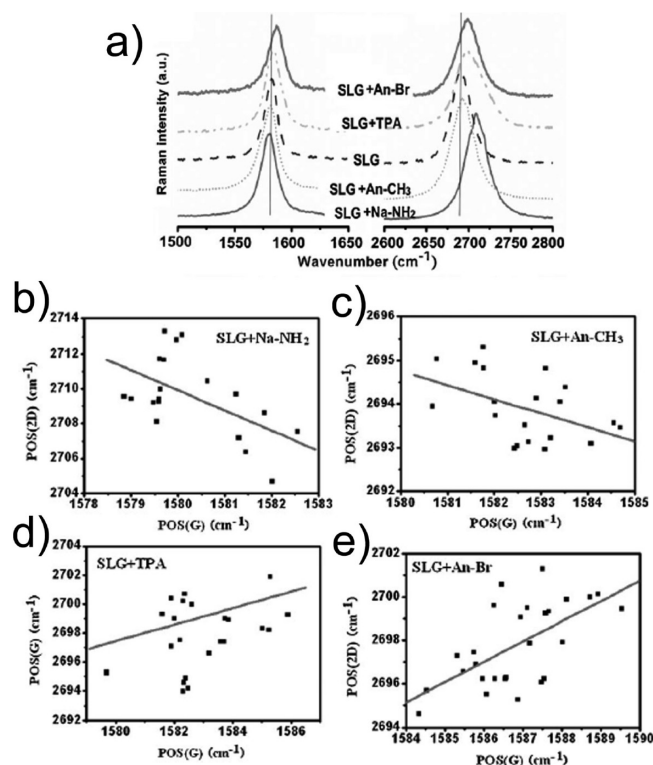


Figure 7. (a) The left is Raman G bands of single layer graphene (SLG) modified without and with different aromatic molecules of Na-NH₂, An-CH₃, TPA, and An-Br. The right is the corresponding Raman 2D bands. (b–e) Curves showing Raman 2D intensity as a function of G intensity for graphenes modified with Na-NH₂, An-CH₃, TPA, and An-Br. (Adapted from ref 49 with permission. Copyright 2009, John Wiley and Sons, Inc.)

the thickness of F4-TCNQ surpasses about 1.0 nm. The observed increase in the work function of graphene is apparently due to the interfacial electron transfer from graphene to F4-TCNQ, generating p-doping of graphene. By using DFT calculations, the electron transfer from graphene to F4-TCNQ was estimated to be about 0.3 electron per molecule.⁴⁴ Considering the fact that the work function of graphene stops increasing after the thickness reaches around 1 nm, the charge separation is likely limited to the interface domain. The result shown in Figure 6 also implies that the charge carrier density within graphene may be modulated by changing the thickness (or density) of the surface stacked molecules.

Similar to the approach as illustrated in Figure 6, n-type graphene can be realized by stacking electron donor molecules on the surface. In such a situation, electrons are transferred from the stacked molecules to graphene, generating electrons as the major charge carrier. Some aromatic molecules, e.g., PTCDI and vanadyl-phthalocyanine (VOPc) are among the suitable electron donors for stacking with graphene,^{23,42} taking advantage of their large planar π -configuration structure. By changing the reduction potential (essentially the HOMO level) of the electron donor molecules, the n-doping effect of graphene (e.g., the electron density) can thereby be controlled. However, it should be noted that there seems no simple rule that can be applied to the selection of effective doping molecules, although the relative electron affinity of aromatic molecules and graphene is often used to determine the doping type. Many other factors, such as molecular electronic structure and π - π stacking configuration, also affect the efficiency of charge separation.

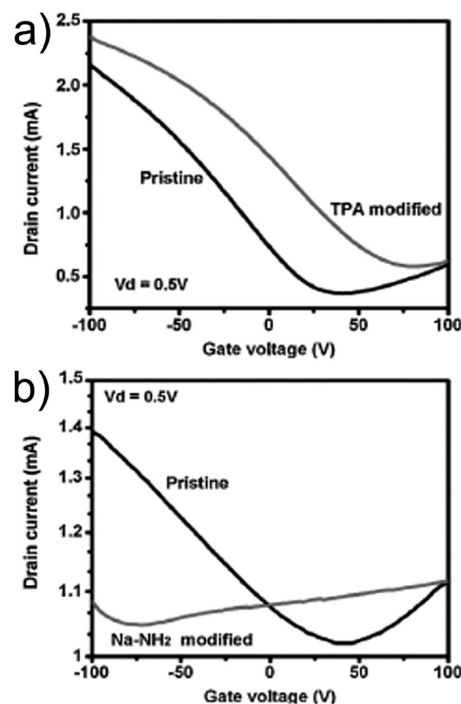


Figure 8. (a) Transfer curves of graphene FET before and after TPA modification. (b) Transfer curves of graphene FET before and after Na-NH₂ modification. (Adapted from ref 49 with permission. Copyright 2009, John Wiley and Sons, Inc.)

p–n junction is a fundamental unit in integrated circuits. By surface stacking of electron donor or acceptor molecules as described above, it is possible to obtain p–n junctions for graphene-based nanoelectronics.^{45,46} The graphene synthesized on SiC substrates is n-type induced by the substrates.⁴⁷ Using the common thermal vapor method, p-dopants, e.g., F4-TCNQ and TCNE, can be assembled onto the surface of graphene, leading to the formation of a molecular scale p–n junction. Depending on the surface density of the molecule coverage, the p–n junction could be localized as defined by the nanojunction domain (basically the size of the molecule), or expand to a large area if strong lateral intermolecular association exists.

The doping effect caused by different aromatic molecules (electron donor vs acceptor) can be examined by Raman spectroscopy,^{48–50} which represents a powerful tool that is highly adaptable and widely used for structural characterization of carbon nanostructures, including CNTs, fullerene, graphene, and their composites. The charge transfer between stacking molecules and graphene can shift the Fermi energy level in graphene, thus resulting in significant change of the G and 2D Raman bands of graphene.

Figure 7a shows the typical Raman G and 2D bands of pristine graphene and the ones modified with a series of aromatic molecules, including 1,5-naphthalenediamine (Na-NH₂), 9,10-dimethylanthracene (An-CH₃), 9,10-dibromoanthracene (An-Br), and TPA. The structures of these molecules are illustrated in Scheme 1. Therein, Na-NH₂ and An-CH₃ serve as electron donors, and An-Br and TPA serve as electron acceptors. Regardless of whether it was modified with electron donors or acceptors, the 2D band was always up-shifted compared to the pristine graphene. By contrast, the G band showed different behavior. When modified with electron acceptors, the G band shifted upward, whereas downshift was observed when modified with electron donors. In this situation, the Raman phenomena are dominated by electronic rather than

dynamic effect.⁴⁹ This is consistent with what has been observed for CNTs, for which the origination of the similar Raman effect is usually ascribed to electronic effect,⁵¹ but different from what has been observed in the doping process of graphene induced by electrical or electrochemical gating, wherein the Raman effect is usually dominated by dynamic effect.^{52,53} The major difference should be due to the fact that stacked aromatic molecules induce defects that scatter electrons to nonadiabatic states.

Figure 7b shows the relationship between the Raman G and 2D band frequencies of the same graphene sample modified by Na-NH₂ at different positions. These data points can be roughly linearly fitted exhibiting that the variation in 2D frequency inversely correlates with variation in G frequency. The graphenes modified with the two electron donor molecules exhibit a similar inverse linear relationship (Figure 7b,c), but the graphenes modified with electron acceptors show a proportional linear relationship (Figure 7d,e). This distinct relationship (positive or negative slope) may be used to distinguish between n- or p-doped graphene.

The different doping also affects the FET performance of graphene. While graphene is exposed to atmosphere, it is often p-doped induced by oxygen, leading to the neutral point that is present at the positive gate voltage (Figure 8a,b). The doping by electron acceptors (e.g., TPA) or donors (e.g., Na-NH₂) apparently exhibits distinct behavior on the gate modulation. The stacking of TPA molecules decreases the electron density, and thus lowers the Fermi energy level of graphene. This results in upshift of the neutral point from around 30 to 80 V. By contrast, the staking of Na-NH₂ results in downshift from 30 V to -70 V, owing to the fact that the electron injection from Na-NH₂ causes an increase in electron density.

The charge transfer as observed between stacked molecules and graphene may also find some other applications such as photoelectronics and gas sensors. For example, by stacking photosensitive molecules onto graphene, the photoinduced charge separation within the molecules may facilitate the subsequent charge transfer with graphene. Research along this line will likely lead to application in photovoltaics⁵⁴ or high-speed photoswitches. Some aromatic molecules demonstrate strong, selective interaction with explosive molecules (e.g., TNT), and the modulation of the electrical or optical properties thus attained can be employed as a sensor signal for trace vapor detection of explosives and other chemical threats.^{38,55} Modifying graphene with these functional molecules may extend the sensor module into a new scenery, taking advantage of the high conductivity, as well as the large, open area of graphene.⁵⁶

In order to precisely control the electronic properties, particularly tune the band gap of graphene, it is critical to design and synthesize aromatic molecules that are tailorable in structure so as to be suited for changing the interfacial electronic (charge transfer) interaction and the stacking configuration.

Future Issues and Challenges. Stacking aromatic molecules on graphene opens a promising way to tune its electronic properties. However, the study is still in its early stage. In order to precisely control the electronic properties, particularly tune the band gap of graphene, it is critical to design and synthesize aromatic molecules that are tailorable in structure so as to be suited for changing the interfacial electronic (charge transfer) interaction and the stacking configuration. Along with this, researchers will also have to develop a large area surface deposition technique to control the surface density and pattern of stacking, for which self-assembly via solution processing or vapor transfer will likely be the promising way. With the current initial success in stacking induced charge transfer and separation, the immediate issue for the next step of research to address is to control and modulate the charge separation between graphene and the stacked molecules, which in turn can be realized through electrical (gate) or optical effect. The research along this line will pave the way leading to development of the first round of graphene based optoelectronic nanodevices, including (but not limited to) FETs, phototransistors, photovoltaics, and chemical sensors.

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