JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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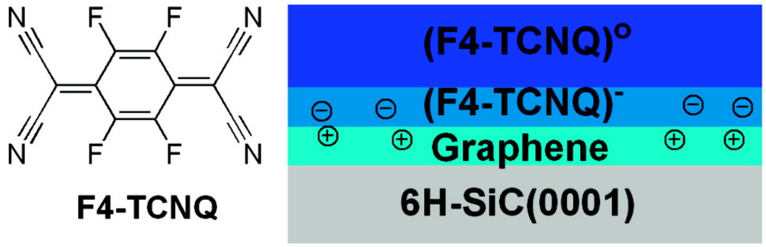
*J. Am. Chem. Soc.*, **2007**, 129 (34), 10418-10422• DOI: 10.1021/ja071658g • Publication Date (Web): 01 August 2007



$e^-$ transferring from graphene to F4-TCNQ

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# Surface Transfer p-Type Doping of Epitaxial Graphene

Wei Chen,* Shi Chen, Dong Chen Qi, Xing Yu Gao, and Andrew Thye Shen Wee*

*Contribution from the Department of Physics, National University of Singapore,*
*2 Science Drive 3, Singapore 117542, Singapore*

Received March 8, 2007; E-mail: phycw@nus.edu.sg; phyweets@nus.edu.sg

***Abstract:*** Epitaxial graphene thermally grown on 6H-SiC(0001) can be p-type doped via a novel surface transfer doping scheme by modifying the surface with the electron acceptor, tetrafluoro-tetracyanoquinodimethane (F4-TCNQ). Synchrotron-based high-resolution photoemission spectroscopy reveals that electron transfer from graphene to adsorbed F4-TCNQ is responsible for the p-type doping of graphene. This novel surface transfer doping scheme by surface modification with appropriate molecular acceptors represents a simple and effective method to nondestructively dope epitaxial graphene for future nanoelectronics applications.

## Introduction

Monocrystalline graphitic films with one or few-layer thickness have attracted much attention recently due to their exotic properties,[1−9] such as the existence of massless Dirac fermions,[1] the quantum Hall effect,[2] and gate control of transport (electron or hole) properties.[3] In particular, it has been demonstrated that ultrathin graphene films epitaxially grown on commercial silicon carbide substrates by thermal decomposition in vacuum can be patterned using standard nanolithography methods,[8,10] making it compatible with current semiconductor technology. Recent transport measurements on ultrathin epitaxial graphene (EG) on silicon carbide (SiC) substrates have revealed the Dirac nature of the charge carriers.[8] Long phase coherence lengths of over 1 $\mu$m at 4 K and mobilities exceeding 2.5 $m^2$ per volt-second have also been observed,[8] making EG a promising material for future nanoelectronics. Electron or hole transport in field-effect devices based on micromechanically cleaved one or few-layer graphite can be controlled by externally applied voltages.[3] For further development of EG nanoelectronics, precise control of carrier type and concentration in EG is desirable. It has been recently shown that n-type carrier concentration in EG can be selectively adjusted by varying the amount of potassium deposited on the EG surface, leading to control of the gap between valence and conduction bands.[9]

Here, we demonstrate p-type doping of EG by surface modification with the molecular electron acceptor, tetrafluoro-tetracyanoquinodimethane (F4-TCNQ). The structure of F4-TCNQ is shown in Figure 1a. F4-TCNQ has been widely used in organic light-emitting diodes to reduce the hole injection barrier by forming a narrow space-charge region near the metal contact, thereby improving device performance.[11−14] By incorporation of F4-TCNQ, precise tuning of the hole concentration (p-type doping) of single-wall carbon nanotubes (SWNTs) field-effect transistors (FETs)[15] and organic semiconductors such as zinc-phthalocyanine (ZnPc)[16,17] has also been demonstrated. Modifying the EG surface with F4-TCNQ is therefore expected to favor electron transfer from EG into F4-TCNQ molecules, leading to an electron accumulation layer in F4-TCNQ and a depletion layer in EG, thereby achieving p-type doping of EG. This charge transfer at the F4-TCNQ/EG interface is illustrated by the schematic in Figure 1b. The hole concentration in EG can be controlled by the surface coverage of F4-TCNQ. Synchrotron-based high-resolution photoemission spectroscopy is used to monitor the charge transfer at the F4-TCNQ/EG interface.

## Experimental Section

Ultrathin epitaxial graphene (EG) was prepared by annealing a chemically etched (10% HF solution) n-type Si-terminated 6H-SiC(0001) sample (CREE Research Inc.) at 850 °C under a silicon flux

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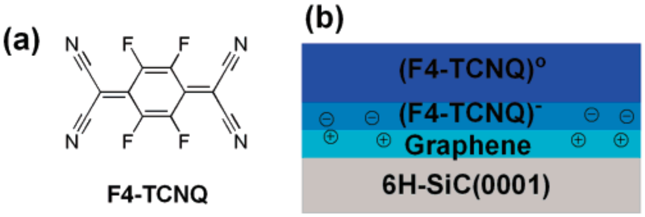

***Figure 1.*** Schematic drawings of (a) structure of tetrafluoro-tetracyanoquinodimethane (F4-TCNQ) and (b) the charge transfer at the F4-TCNQ/graphene interface. Electron transfer from graphene to F4-TCNQ only occurred at the interface, where F4-TCNQ (in direct contact with graphene) is negatively charged and graphene is positively charged. F4-TCNQ in multilayers remains its neutral state (uncharged).

for 2 min in an ultrahigh vacuum (UHV), resulting in a Si-rich 3 × 3-reconstructed surface,[18,19] and subsequently annealing the sample several times at 1300 °C in the absence of the silicon flux to form EG.[8−10,18,20] The structure of EG was confirmed by in-situ low-energy-electron-diffraction (LEED) and angle-resolved photoemission spectroscopy (PES). The thickness of the ultrathin EG layer ranged from 1 monolayer to 3 layers of graphene sheet, as measured by monitoring the attenuation of the bulk SiC related Si 2p PES signal (details can be found in the Supporting Information). The PES experiment was carried out at the Surface, Interface and Nanostructure Science (SINS) beamline and endstation of the Singapore Synchrotron Light Source (SSLS).[21,22] The binding energies of all PES spectra were normalized to the Fermi level of the electron energy analyzer. The intensities of all of the spectra were normalized to the total incoming photon flux measured with a gold grid. Vacuum level shift was determined from PES spectra at the low-kinetic energy onset (secondary electron cutoff) using a photon energy of 60 eV with −5 V sample bias. Sample work functions ($\phi$) were obtained through the equation of $\phi = h\nu - W$, where $W$ is the spectrum width (the energy difference between the substrate Fermi level and low kinetic energy onset).[23] The work function of the electron analyzer was measured to be 4.30 ± 0.05 eV. F4-TCNQ and $C_{60}$ molecules (Sigma-Aldrich) were evaporated in situ from a low-temperature Knudsen cell (MBE-Komponenten, Germany) onto EG at room temperature in the main UHV chamber. The nominal thickness of F4-TCNQ and $C_{60}$ was estimated by monitoring the attenuation in intensity of the Si 2p peak of bulk SiC before and after deposition.[24] The experiment was performed with sequential deposition/measurement stages. To avoid the photon beam damage on the F4-TCNQ and $C_{60}$ molecules, low total beam current of the incoming synchrotron light was used during the experiment by adjusting the beam exist slit; for example, the beam current was maintained below 3 nA for photon beam energy of 500 eV (core levels), and 0.6 nA for 60 eV photon beam (valance band). The photon beam damage to the F4-TCNQ and $C_{60}$ molecules was further checked by monitoring the core-level peaks as well as the valence band structures of the molecules after long time exposure to the synchrotron beam (more than 2 h). After exposure, we did not observe any apparent change in the core-level peaks and the valence band structures, confirming the negligible photon beam damage under low beam current.

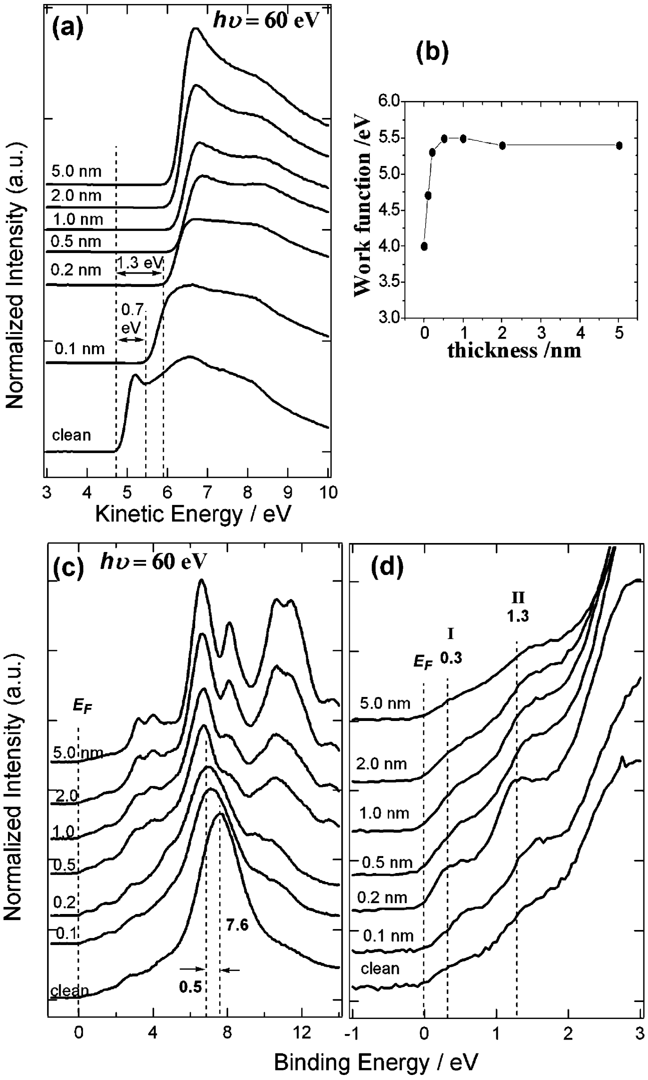

***Figure 2.*** Synchrotron PES spectra during the deposition of F4-TCNQ on EG: (a) PES spectra at the low-kinetic energy part (secondary electron cutoff), (c) valence band spectra at the low-binding energy part, and (d) corresponding near the $E_F$ region spectra from panel (c). All spectra are measured with a photon energy of 60 eV. (b) The plot of the sample work function of EG as a function of the F4-TCNQ coverage.

## Results and Discussion

The charge transfer at the F4-TCNQ/EG interface was monitored by synchrotron-based high-resolution photoemission spectroscopy (PES). Figure 2 shows the evolution of PES spectra at the low-kinetic energy region [Figure 2a] and valence band spectra at the low-binding energy region [Figure 2c and d] during the deposition of F4-TCNQ on EG. The vacuum level of EG upon the deposition of F4-TCNQ was measured by linear extrapolation of the low-kinetic energy onset (secondary electron cutoff) of PES spectra. After the deposition of 0.1 nm F4-TCNQ, the work function increased from 4.0 eV (clean EG) to 4.7 eV, or an upward shift of vacuum level by 0.7 eV as shown in Figure 2a. The work function shift increased to 1.3 eV when the thickness was 0.2 nm. The changes in sample work function with F4-TCNQ thickness are plotted in Figure 2b. It is known that the sample work function of inert substrates such as graphite

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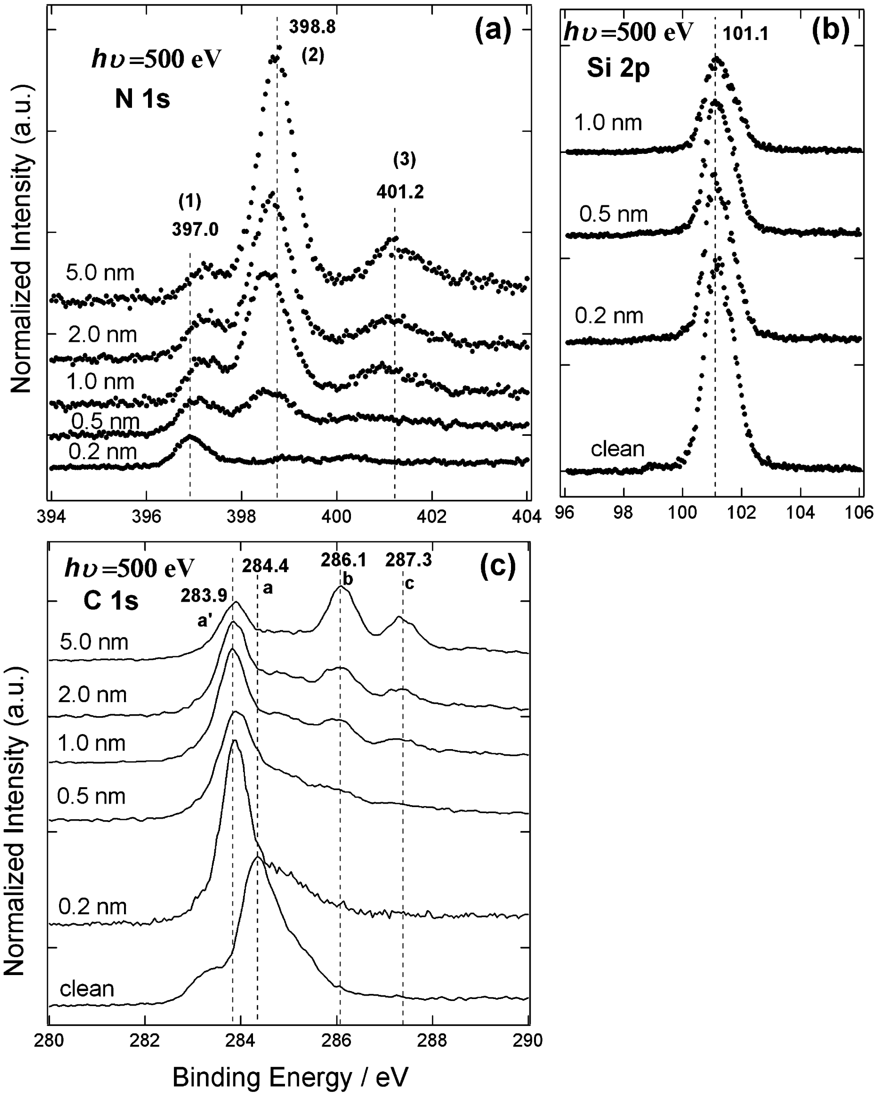

***Figure 3.*** Synchrotron PES core level spectra during the deposition of F4-TCNQ on EG: (a) N 1s, (b) Si 2p, and (c) C 1s. All spectra are measured with a photon energy of 500 eV.

(excluding metal substrates) is extremely sensitive to interfacial charge transfer, and an upward shift of vacuum level or increase in sample work function occurs if electrons transfer from the substrate to the adsorbate overlayer.[23,25] As proposed in Figure 1b, the strong electron-accepting characteristic of F4-TCNQ favors electron transfer from EG into F4-TCNQ, creating an interface dipole, which causes an upward shift of vacuum level or increase in sample work function. In the valence band spectrum [Figure 2d], two new peaks at binding energies of 0.3 eV (peak I) and 1.3 eV (peak II) appear. Similar electron transfer has been previously observed at the F4-TCNQ/Au interface.[25a] Peak I (lower binding energy peak) is assigned to the (partially) filled lowest-unoccupied-molecular-orbital (LUMO) and peak II (higher binding energy peak) to the relaxed highest-occupied-molecular-orbital (HOMO) of F4-TCNQ after electron transfer from EG to F4-TCNQ.[25a] Both peaks gradually disappear at higher F4-TCNQ thickness, accompanied by an almost unchanged sample work function or vacuum level [Figure 2a and b]. This indicates that electron transfer only occurs at the F4-TCNQ/EG interface and the bulk F4-TCNQ film remains largely uncharged.

In Figure 3, representative PES spectra of N 1s [Figure 3a], Si 2p [Figure 3b], and C 1s [Figure 3c] are shown as a function of F4-TCNQ thickness on EG. After deposition of 0.2 nm F4-TCNQ, N 1s is dominated by the component [peak (1)] centered at a binding energy of 397.0 ± 0.05 eV. Upon increasing the thickness to 0.5 nm, a new component [peak (2)] at a higher binding energy of 398.8 ± 0.05 eV appears. Further deposition leads to an intensity increase in peak (2) and a gradual attenuation of peak (1). By comparison with F4-TCNQ on Au,[25a] peak (2) is assigned to neutral bulk F4-TCNQ, and peak (1) to the negatively charged F4-TCNQ in direct contact with EG where significant charge transfer occurs. Peak (3) at a binding energy of 401.2 ± 0.05 eV is attributed to shakeup processes.[26] The evolution of N 1s spectra during the deposition of F4-TCNQ on EG supports our hypothesis of electron transfer from EG to F4-TCNQ at the interface.

For the C 1s spectrum of the clean surface, the EG-related C 1s component (peak a) is centered at a binding energy of 284.4 ± 0.05 eV; the lower binding energy shoulder is attributed

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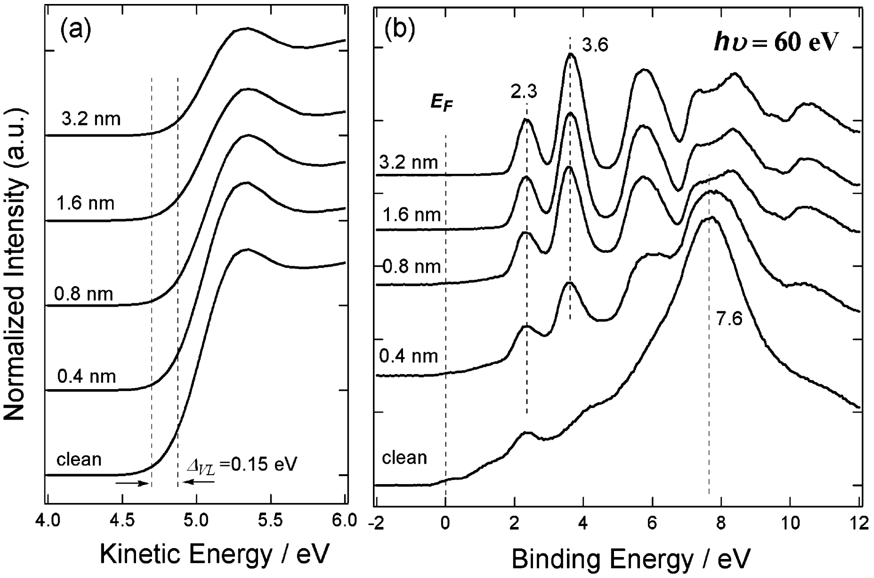

***Figure 4.*** Synchrotron PES spectra during the deposition of $C_{60}$ on EG: (a) PES spectra at the low-kinetic energy part (secondary electron cutoff) and (b) valence band spectra at the low-binding energy part.

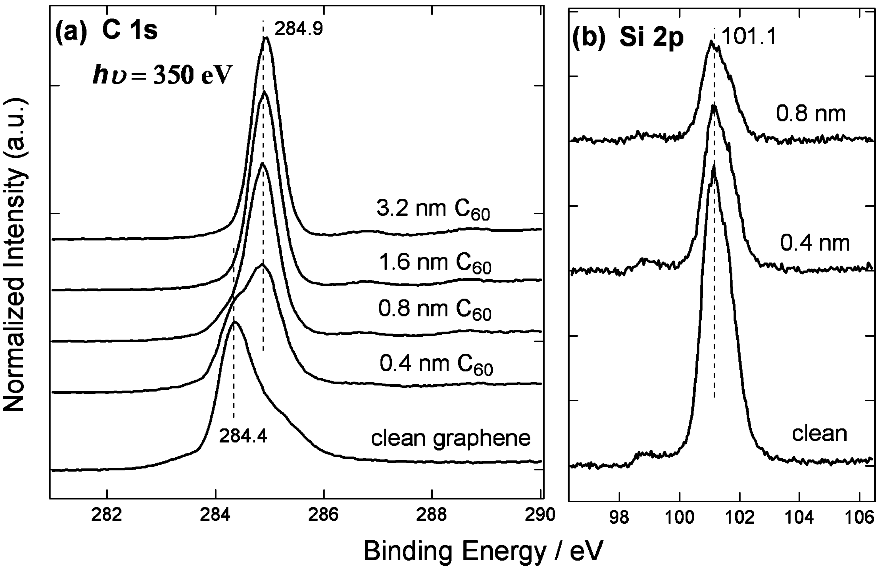

***Figure 5.*** Synchrotron PES core level spectra during the deposition of $C_{60}$ on EG: (a) C 1s and (b) Si 2p. All spectra are measured with a photon energy of 350 eV.

to the bulk SiC-related component, and higher binding energy shoulder to the so-called "$6\sqrt{3} \times 6\sqrt{3}$ *R*30°" or carbon nanomesh related components buried under EG.[18,27] After deposition of 0.2 nm F4-TCNQ, a 0.5 eV shift of the EG-related C 1s component (peak a) to lower binding energy part (peak a′) is observed. At higher thicknesses, the binding energy of peak a′ remains constant, while the peak intensity is gradually attenuated. Two new peaks, peak b at 286.1 ± 0.05 eV and peak c at 287.3 ± 0.05 eV, appear at higher thicknesses and are assigned to F4-TCNQ related C 1s components. The shift of peak a to lower binding energy can be explained by the upward band bending in EG due to increased hole concentration or p-type doping of EG. This band bending in EG is also seen in the valence band spectra [Figure 2c], where the EG-related valence state (7.6 ± 0.05 eV) is shifted to lower binding energy by 0.5 eV at 0.2 nm F4-TCNQ coverage. The band bending due to the electron transfer at the F4-TCNQ/EG interface does not occur in bulk SiC as the Si 2p peak remains at constant binding energy during F4-TCNQ deposition [Figure 3b], indicating that the holes are mainly confined within the EG.

In contrast to F4-TCNQ (stronger electron acceptor with electron affinity of about 5.2 eV),[28] the adsorption of another molecular acceptor of $C_{60}$ (weaker electron acceptor with electron affinity of about 3.7 eV)[29] does not result in a significant charge transfer at the $C_{60}$/EG interface. In Figure 4a and b, representative PES spectra at the low-kinetic energy region and the low-binding energy region are shown as a function of $C_{60}$ thickness, respectively. As shown in Figure 4a, an upward shift of the vacuum level by 0.15 ± 0.05 eV is observed after deposition of 0.8 nm $C_{60}$, revealing that a very weak charge

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transfer occurs at the $C_{60}$/EG interface involving electrons transferring from EG to the $C_{60}$ overylayer. At the same time, the $C_{60}$ HOMO (highest-occupied-molecular-orbital) locates with the binding energy at 2.5 ± 0.05 eV [Figure 4b]. At 3.2 nm $C_{60}$ coverage, the typical valence band spectrum of fullerene is observed without any apparent contribution from the EG substrate.[30,31] Figure 5 shows the evolution of C 1s and Si 2p peaks during the deposition of $C_{60}$ on EG. The photon energy of 350 eV was chosen here to enhance the surface sensitivity. With increasing amounts of $C_{60}$ to 0.4 nm, the C 1s peak is extended to the lower binding energy part at 284.9 ± 0.05 eV [Figure 5a], which is attributed to the photoexcitation of $C_{60}$.[32,33] This $C_{60}$-related component dominates the C 1s peak after increasing the coverage to 0.8 nm. After increasing the coverage to 3.2 nm, the binding energy of C 1s remains constant at 284.9 ± 0.05 eV. At the same time, neither a binding energy shift of Si 2p nor a new Si 2p component at different $C_{60}$ coverages is observed [Figure 5b]. It suggests that no covalent or ionic bonding occurs at the $C_{60}$/EG interface. Unlike the deposition of F4-TCNQ that causes the shifts toward lower binding energy of the EG-related C 1s [Figure 3c] and HOMO [Figure 2c] peaks, we do not observe any apparent shifts of the C 1s or the HOMO peak due to the surface-transfer doping induced band-bending after modifying the EG surface with $C_{60}$, confirming that adsorption of weak electron acceptor of $C_{60}$ does not result in a significant surface transfer p-type doping of EG layers.

## Conclusion

In conclusion, this work demonstrates a simple and effective way to nondestructively control the hole concentration in epitaxial graphene (EG) layers thermally grown on 6H-SiC-(0001) by modifying the EG surface with an appropriate electron acceptor of tetrafluoro-tetracyanoquinodimethane (F4-TCNQ). Synchrotron-based high-resolution photoemission spectroscopy study clearly reveals that electron transfer from graphene to adsorbed F4-TCNQ is responsible for the p-type doping of graphene. In contrast, the adsorption of a relatively weak molecular acceptor of $C_{60}$ does not result in a significant charge transfer at the $C_{60}$/EG interface, and hence the absence of the surface transfer doping of the EG layers. This novel surface transfer doping scheme by surface modification with appropriate molecular acceptors has great implications for future EG-related nanoelectronic devices.

**Acknowledgment.** W.C. acknowledges the support from an LKY PDF fellowship. We acknowledge support from A*STAR grant R-398-000-036-305 and ARF grant R-144-000-196-112.

**Supporting Information Available:** Method used to determine the thickness of the ultrathin epitaxial graphene layer used in our experiment. This material is available free of charge via the Internet at http://pubs.acs.org.

JA071658G

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