Supplementary Information:

Graphene field effect transistor as a probe of electronic structure and charge transfer at organic molecule-graphene interfaces

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Density functional theory (DFT) calculations

To gain a theoretical insight in the observed effects, we performed density functional theory (DFT) calculations of triazine and melamine on graphene using the Vienna *ab-initio* simulation package (VASP) [1-4]. We used the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) for electron exchange-correlation functional [5]. The core and valence electrons were treated using projector augmented wave (PAW) scheme [6] with an energy cut-off of 400 eV. We used a semiempirical functional developed by Grimme (DFT-D2) [7] to account for van der Waals interactions in the weakly bound system.

We first optimized the hexagonal primitive structure of graphite (a = 2.456 Å, c = 6.696 Å) using Gamma-centered Monkhorst-Pack grid [8] with a reciprocal space k-point setting of 20×20×20. This yielded an optimized lattice parameter of a = 2.459 Å, c = 6.161 Å. Next, we exfoliated a single layer of graphene from this system and constructed 4×4 and 7×7 supercells, upon which we placed a Bernal stacked single molecule of triazine and melamine. This geometry has been found to have the lowest binding energy from all considered geometries (Figure S01). A gamma-centered grid with a reciprocal space k-point setting of 3×3×1 was used for these systems. The periodic images were separated by a 20 Å vacuum space in the z-direction, which was large enough to avoid interactions between the graphene layers. All structures were relaxed until the electronic energy converged to 10^{-6} eV and forces on all atoms converged to 10^{-4} eV/Å.

Charge analysis and assignment was performed using the Bader atom-in-molecules method [9]. This method divides up electronic density into partitions whose boundaries are defined as regions where the normal component of density gradient is zero. Integrating these partitions yields the partial charge of the enclosed atom.

XPS and NEXAFS

Synchrotron XPS and NEXAFS experiments were conducted in an ultra-high vacuum (UHV) chamber (base pressure of 1×10^{-10} mbar) at the Soft X-ray beamline at the Australian Synchrotron. Photon energies were chosen to ensure maximum surface sensitivity for high resolution core level scans of C1s (hν = 330 eV) and N1s (hν = 500 eV). The binding energy (BE) scale of all XPS spectra was referenced to the Fermi energy by setting the BE of the 4f 7/2 core level of a clean Au reference substrate to a value of 84.00 eV. Core level XPS spectra were analyzed after background removal using a Shirley background subtraction and peak fitting with a series of Voigt functions. NEXAFS measurements were made in partial electron yield (PEY) mode to maximize the surface sensitivity and achieve a good correlation with the XPS experiments. All NEXAFS spectra were processed through standard pre- and post-edge normalization methods [10], allowing intensity and energy comparison across different scans. Carbon K-edge NEXAFS spectra required double normalization due to the presence of carbon contamination on mirrors in the beamline. Therefore the sample signals (I_{sample}) of the PEY spectra were normalized to the flux curve (I_0) which was detected by measuring the photocurrent from a gold mesh mounted behind the exit slit of the monochromators. PEY sample current was further normalized to signals measured on a Si photodiode in the analysis chamber.

Melamine (99%) and s-triazine (97%) powders were sourced from Sigma Aldrich. Organic layers were deposited in situ (1×10^{-9} mbar) by sublimation on the graphene substrate. Deposition of the molecules on graphene samples was performed using a low temperature effusion cell (MBE Komponenten GmbH) operating at 140 and 175 °C, respectively. Increasing melamine coverage was achieved by incremental molecular depositions on graphene at room temperature between each XPS and electronic measurement. Since triazine desorbs from graphene at room temperature, we controlled the molecular coverage of triazine by depositing a thick layer at -100 ºC and performed the measurements while triazine slowly desorbed off the graphene surface. Molecular adlayer thicknesses were monitored by QCM and measured by considering the attenuation of the substrate signal in C1s and N1s spectra and determined using the following ratio between the XPS peak areas of the N1s peak corresponding to a monolayer molecular coverage and the C1s peak area of single layer graphene

$$\frac{A_{N1s}}{A_{C1s}} = \frac{n_N \sigma_N(500\ eV) I(500\ eV)}{n_C \sigma_C(330\ eV) I(330\ eV)}$$

where n_N/n_C is a geometric factor representing the ratio of the density of molecular nitrogen atoms to graphene carbon atoms, σ is the cross section of the element at a specific photon energy taken from the NIST database and I is the intensity of photons incident on the sample at a specific photon energy. The C1s and N1s spectra were taken at similar kinetic energy to ensure the analyzer transmission intensity was comparable for each peak. To estimate the ratio of molecular nitrogen to graphene carbon n_N/n_C we used the molecular unit cell sizes of monolayer coverage of triazine and melamine on graphene measured by scanning tunneling microscopy [11,12].

Since the exposure of melamine and triazine to synchrotron radiation can lead to molecular damage, we have extensively examined the effects of damage to the molecules and graphene arising from exposure to synchrotron radiation. To minimize the molecular dissociation in the present study, each C1s core-level spectrum was collected over a short time period (no greater than 5 min) and each XPS measurement was done on a previously unmeasured spot of the graphene sample.

NEXAFS is a powerful tool to determine molecular orientation of adsorbed molecular layers by changing the incident angle of the synchrotron light *E*-vector to the surface plane [10,13]. We collected NEXAFS spectra at five different angles by rotating the sample holder with respect to the incident beam in the plane of incidence. The angle dependent carbon and nitrogen K-edge NEXAFS spectra of the as-prepared graphene and with deposited melamine layers on graphene are shown in Fig. S05-07. The details of the method used to determine the angle of adsorbed molecular layers in respect to the graphene substrate can be found in References [10,13].

Literature

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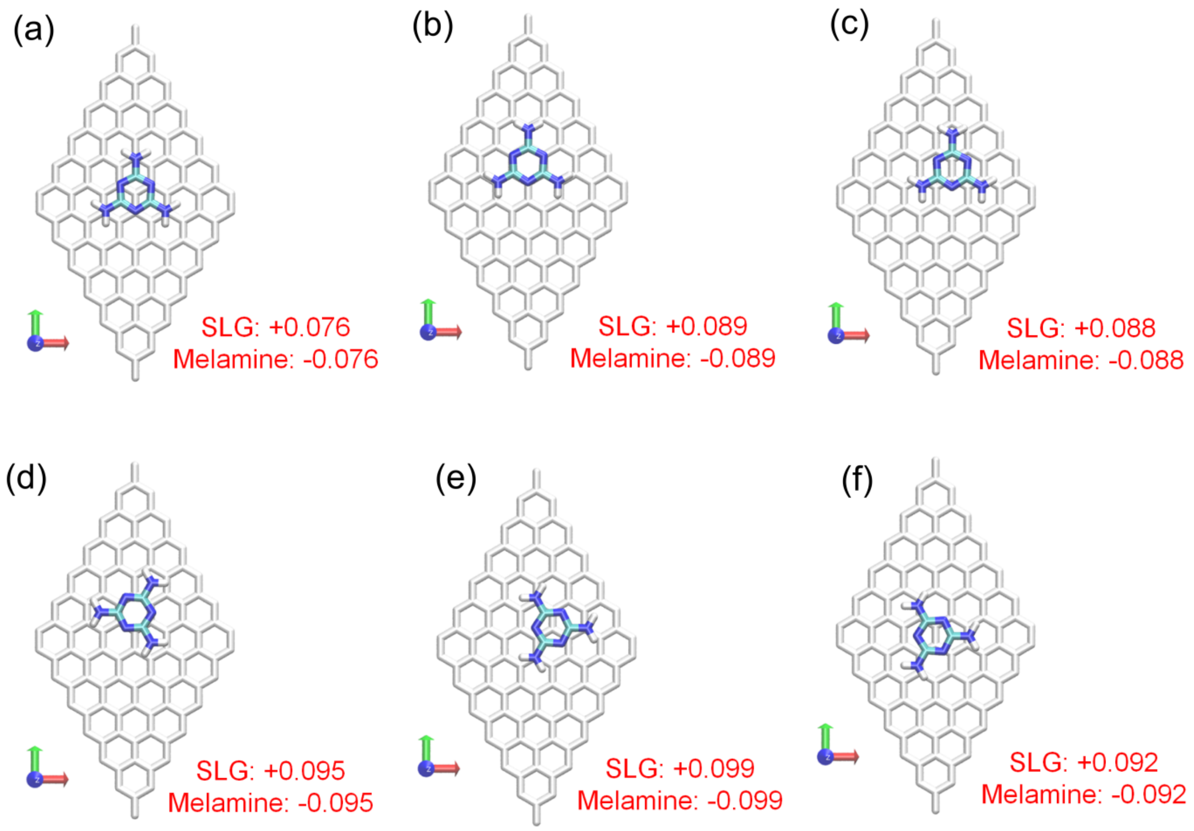

Figure S01. Different adsorption geometries of melamine on graphene and their corresponding charge transfer between melamine and single layer graphene (SLG). The units are in electrons per molecule.

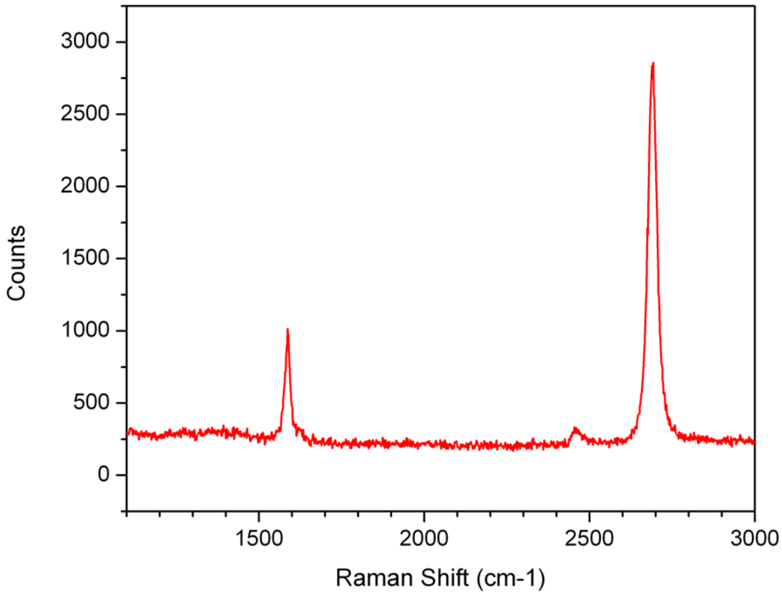

Figure S02. Raman spectroscopy of single layer graphene on SiO_2/Si using a 514 nm excitation laser.

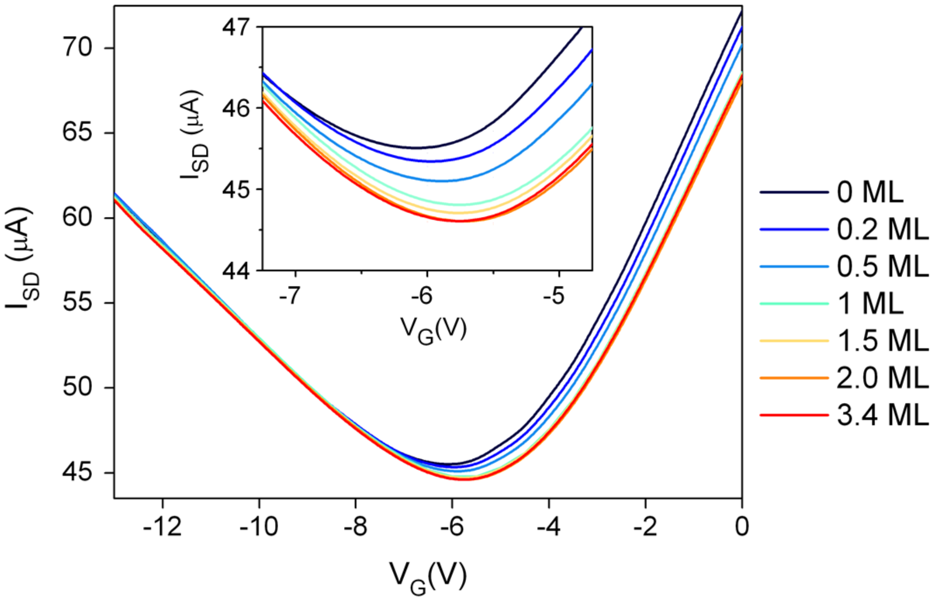

Figure S03. Gate voltage dependent source-drain current (I_{SD}) spectra of a graphene FET at a constant source voltage (V_{SD} = 50 mV) as a function of increasing triazine coverage. The inset shows a positive shift of the conductivity minimum (Dirac point) upon adsorption of triazine, corresponding to *p*-type doping of graphene by triazine.

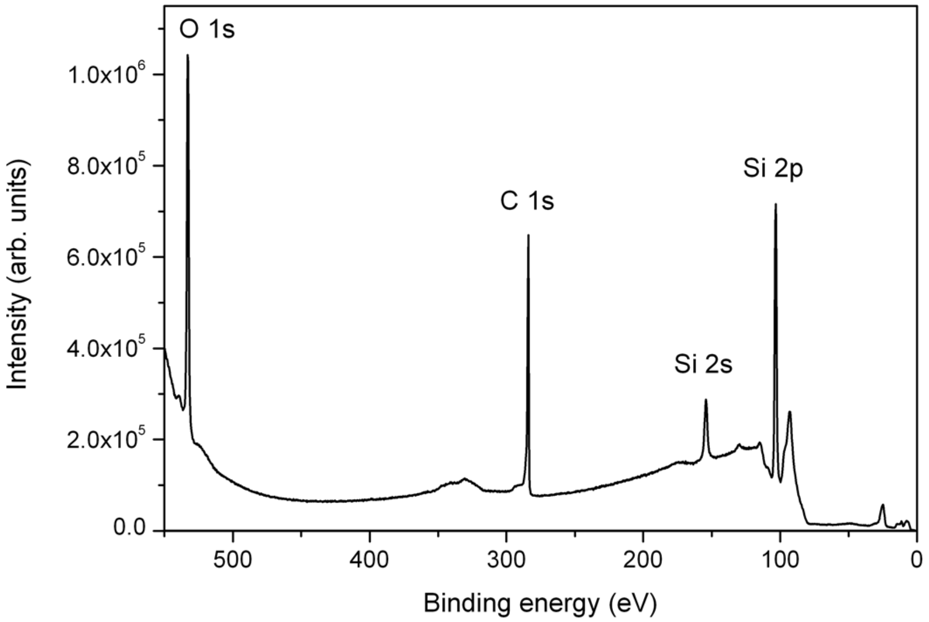

Figure S04. XPS survey spectrum of clean graphene on SiO_2 ($h\nu$ = 600 eV).

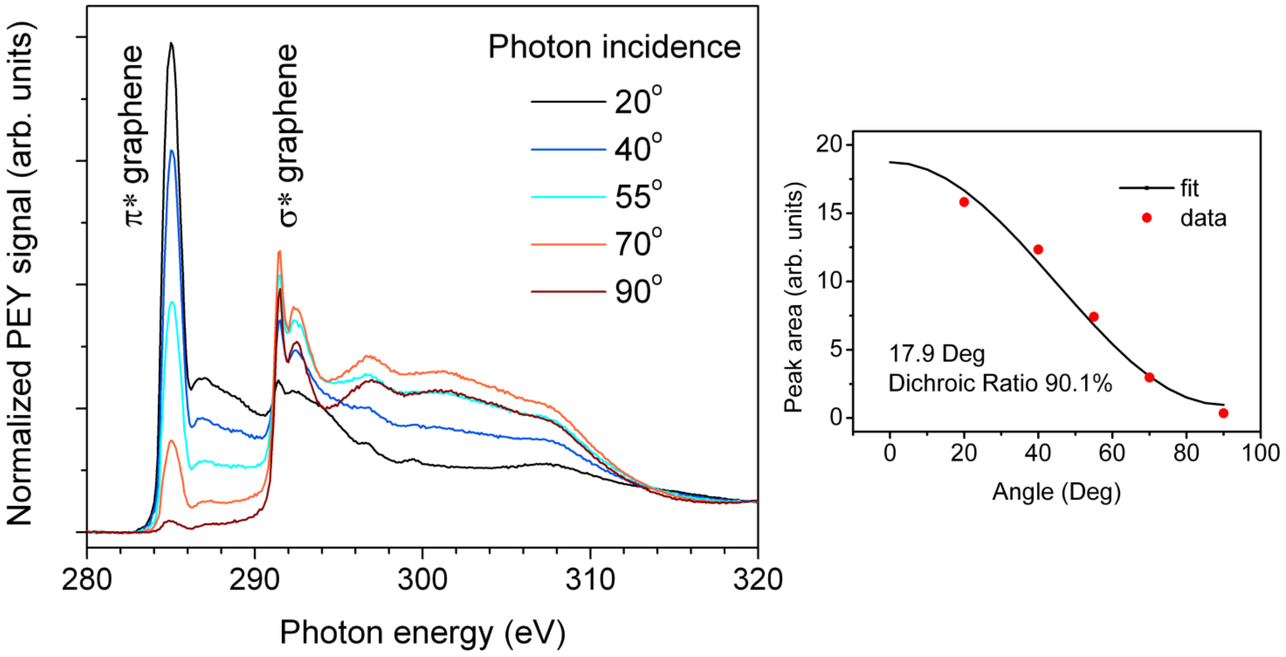

Figure S05. Angle dependent carbon K-edge NEXAFS of graphene on SiO_2 used for the determination of the geometry of graphene layers (C π* vector orbitals) in respect to the electric field of the incident X-ray irradiation.

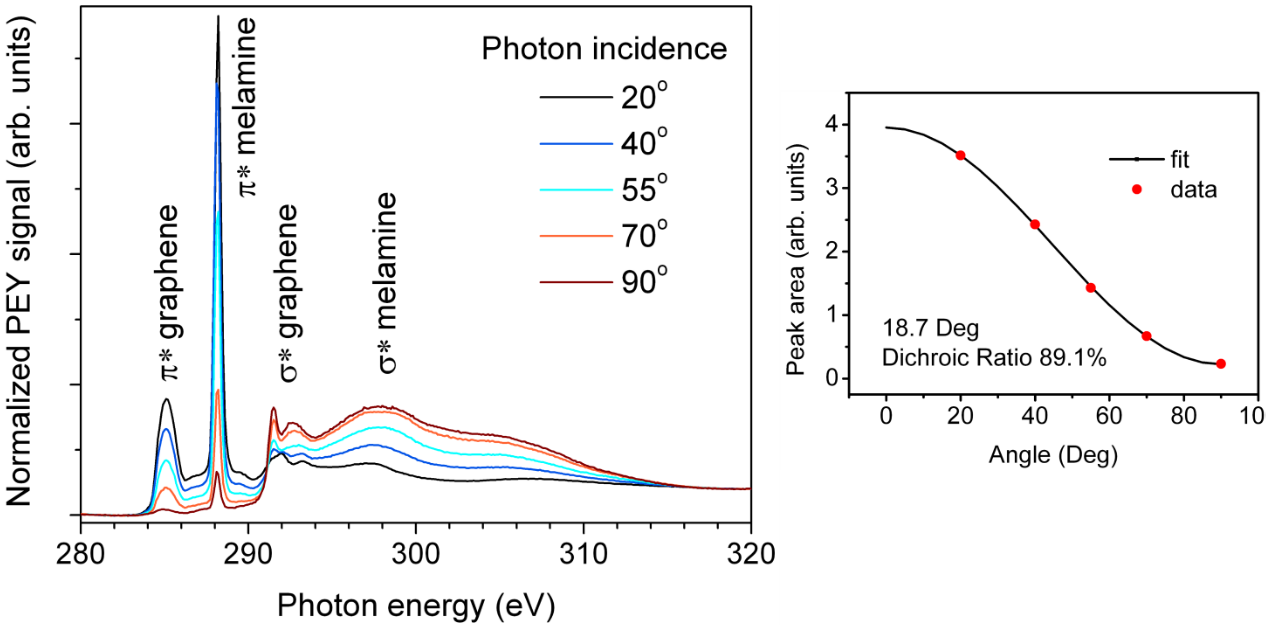

Figure S06. Angle dependent carbon K-edge NEXAFS of 3.6 ML melamine on graphene and determination of the geometry of melamine layers on graphene from molecular C π* vector orbitals plotted with respect to the angle of the electric field of the incident X-ray irradiation with respect to the surface normal.

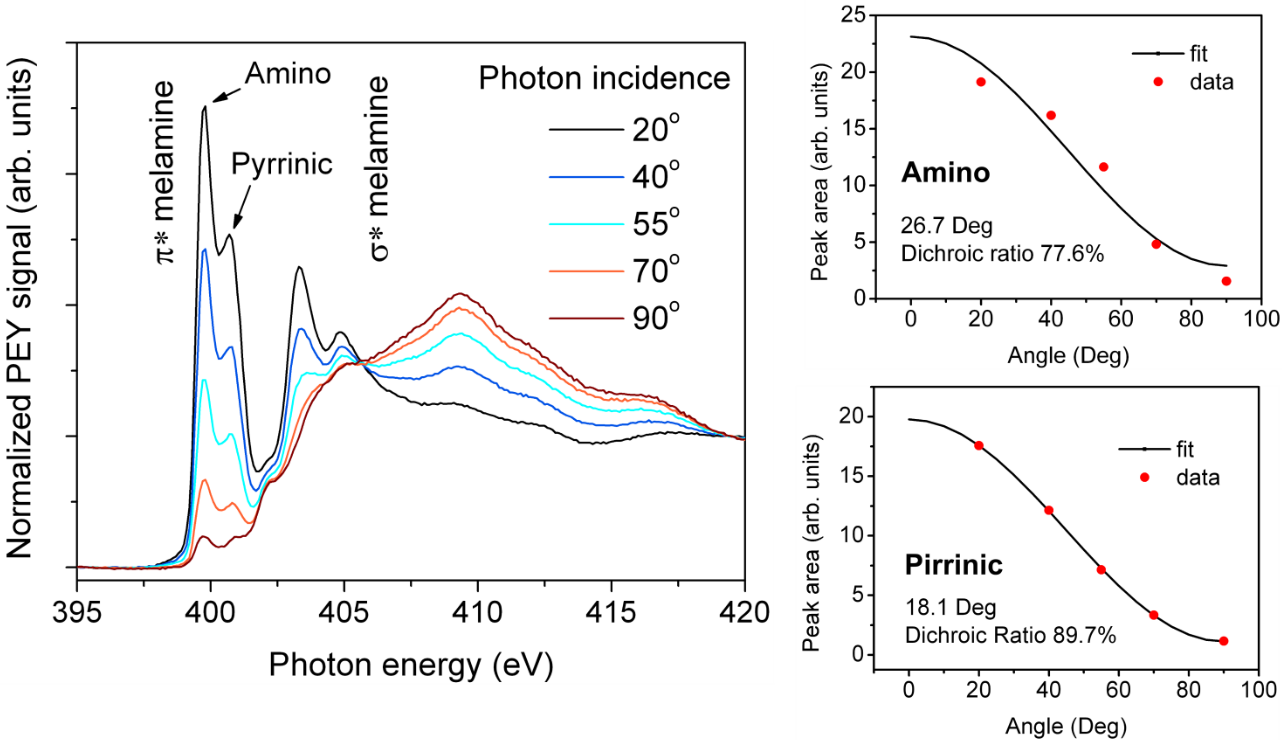

Figure S07. Angle dependent nitrogen K-edge NEXAFS of 3.6 ML melamine on graphene and determination of the geometry of melamine layers on graphene from molecular N π* vector orbitals in respect to the electric field of incident X-ray irradiation.