Supplementary Information 1

Evaluation of structure and composition of graphene/ $C_{60}F_{48}$ assemblies from XPS core-level intensity data

1.1 Evaluation of relative photoemission intensities from a stack of alternating *n* graphene sheets and *m* acceptor layers in graphene/ $C_{60}F_{48}$ assemblies

Define:

$r_{vdW,A}$ outer van der Waals radius of acceptor molecule. For $C_{60}F_{48}$, this is 6.55 Å

r_{C60} radius of C_{60} cage in acceptor molecule. For $C_{60}F_{48}$, this is 3.75 Å

$r_{vdW,A'}$ inner van der Waals radius of acceptor molecule. For $C_{60}F_{48}$, this is 2.1 Å

n_G carbon density, number of atoms per unit area of graphene sheet. Area of single graphene carbon atom, $n_G^{-1} = 2.60$ Å^2

n_A acceptor density, number of acceptor molecules per unit area of graphene sheet

N_{G*} eclipsed number of carbon atoms per acceptor molecule. N_{G*} is given by the van der Waals cross sectional area of acceptor ($\pi\, r_{vdW,A}^2$) to the area of single graphene carbon atom (n_G^{-1}). For $C_{69}F_{48}$, this is 135/ 2.60 = 51.9

N_A number of carbon atoms per acceptor molecule. For $C_{60}F_{48}$, this is 60

$\xi_{G,x}$ photoemission transmission factor for the specified core level x through a graphene overlayer ($0 \le \xi_{G,x} \le 1$). The ratio of intensity of photoemission x of a specie located below the graphene layer to one located above it is $\xi_{G,x}$

$\xi_{A,x}$ photoemission transmission factor for the specified core level x through the van der Waals cross section of an acceptor molecule ($0 \le \xi_{A,x} \le 1$). The ratio of intensity of photoemission x of a specie located below the acceptor layer to one located above it is $\xi_{A,x}$

$\eta_{G,x}$ photoemission self-transmission factor for the specified core level x of graphene ($0 \le \eta_{G,x} \le 1$). The ratio of intensity of photoemission x of an atom of graphene to the same atom in free space is $\eta_{G,x}$

$\eta_{A,x}$ photoemission self-transmission factor for the specified core level x of acceptor molecule ($0 \le \eta_{A,x} \le 1$). The ratio of intensity of photoemission x of an atom of the acceptor to the same atom in free space is $\eta_{A,x}$

ψ_x photoemission rate from the specified core level x of an atom in free space

λ_x phenomenological (bulk) photoelectron inelastic mean free path for specified core level x

n total number of graphene sheets

m total number of acceptor layers $m \in \{n-1, n\}$

i summation index, $i = 1$ for lowest layer, whether graphene or acceptor

Aligned acceptor ($\alpha\alpha$) model. Arrays of acceptor molecules are aligned in vertical columns across different graphene sheets. The bottommost layer is graphene,

Graphene emission intensity:

$$I_{G,x} = \psi_x \eta_{G,x} \sum_{i=1}^{n} \xi_{G,x}^{n-i} [(n_G - N_{G*} n_A) + \xi_{A,x}^{m-i+1} (N_{G*} n_A)] \qquad \text{Eq[S1-1]}$$

Acceptor emission intensity:

$$I_{A,x} = \psi_x \eta_{A,x} \sum_{i=1}^{m} \xi_{G,x}^{n-i} \xi_{A,x}^{n-i} [N_A n_A] \qquad \text{Eq[S1-2]}$$

Random/ staggered acceptor (ran) model. Arrays of acceptor molecules are randomly stacked or stacked in staggered configurations across different graphene sheets. In the dilute limit, with the bottommost layer graphene,

Graphene emission intensity:

$$I_{G,x} = \psi_x \eta_{G,x} \sum_{i=1}^{n} \xi_{G,x}^{n-i} [(n_G - (m-i+1) N_{G*} n_A) + \xi_{A,x} (m-i+1) (N_{G*} n_A)] \qquad \text{Eq[S1-3]}$$

Acceptor emission intensity:

$$I_{A,x} = \psi_x \eta_{A,x} \sum_{i=1}^{m} \xi_{G,x}^{n-i} [N_A n_A]$$ Eq[S1-4]

Data treatment. The following data sets were analyzed.

(a) The dependence of $I_{A.C1s}$/ $I_{G.C1s}$ on stack index was fitted to Eq[S1-2]/ Eq[S1-1] and Eq[S1-4]/ Eq[S1-3] for the $\alpha\alpha$ and ran models, respectively, to evaluate the parameters $\xi_{G,C1s}$, $\xi_{A,C1s}$ and n_A.

(b) The dependence of $I_{A,F1s}$ on stack index was fitted to Eq[S1-2] and Eq[S1-4] for the $\alpha\alpha$ and ran models, respectively, to evaluate the parameters $\xi_{G,F1s}$ and $\xi_{A,F1s}$.

(c) The dependence of $I_{G,C1s}$ on stack index was fitted to Eq[S1-1] and Eq[S1-3] for the $\alpha\alpha$ and ran models, respectively, to evaluate the parameters $\xi_{G,C1s}$ and $\xi_{A,C1s}$ and n_A.

The lower stacks 1–0, 1–1 and 2–1 do not discriminate between the $\alpha\alpha$ and ran models. They are thus used to establish $\xi_{G,C1s}$, $\xi_{A,C1s}$ and n_A. The higher stacks 2–2, 3–2 and 3–3 do however discriminate between the structural models, because of the possibility for eclipsed or staggered stacking for two or more acceptor layers. Therefore they are used to identify the appropriate structural model.

Self-consistency was achieved for the $\alpha\alpha$ model, as shown by the excellent match between model and experimental data (Figure 1c, main paper). The parameter values are summarized in Table S1-1. $\xi_{G,x}$ was reliably determined from the fitting to be 0.45 ±0.03. The attenuation of the photoemissions (both C1s and F1s) of the underlying acceptor layer by the overlying acceptor layer is severe, as shown by stack 2–2 *cf* 1–1, and 3–3 *cf* 2–2 (Figure 1c, main report). From this, $\xi_{A,x}$ was evaluated to be 0.66 ±0.04. To improve confidence in the results, we evaluated theoretical expectations for $\xi_{G,x}$, $\xi_{A,x}$ and $\eta_{A,x}$ / $\eta_{G,x}$ (see Supplementary Information 1.2–1.5). In particularly, both $\xi_{A,x}$ and $\eta_{A,x}$ / $\eta_{G,x}$ agree remarkably well with theory for the expected $\lambda \sim 20$ Å. This together with the greatly over-determined model, lends strong confidence to the analysis.

Parameter	Value
$\xi_{G,C1s}$	0.45 ±0.03
$\xi_{A,C1s}$	0.66 ±0.04
λ_{C1s}	20 ±3
$\eta_{A,C1s}/\ \eta_{G,C1s}$	0.83 ±0.04
n_A	1.8 (±0.1) x 10^{13} cm^{-2}

Table S1-1. Best-fit parameter values for the $\alpha\alpha$ model.

1.2 Dependence of photoelectron transmission factor $\xi_{A,x}$ for $C_{60}F_{48}$

In the continuum approximation, attenuation of the elastic photoemission is determined by the effective material thickness through which the photoelectron passes. From PM3 molecular modeling, the outer van der Waals radius $r_{vdW,A}$ given by the outer edge of the fluorine atoms is 6.55 Å, and the radius of the C_{60} cage r_{C60} is 3.75 Å. The inner van der Waals radius $r_{vdW,A'}$, given by the inner edge of the π orbitals, is 2.1 Å. Thus we model $C_{60}F_{48}$ as a uniform hollow sphere with inner radius 2.1 Å and outer radius 6.55 Å. For vertical photoemission through this shell in the area underneath the van der Waals cross sectional area of the acceptor,

$$\xi_{A,x} = \frac{1}{\pi r_{vdW,A}^{\,2}} \int_0^{r_{vdW,A}} exp(-\frac{h}{\lambda_x}) 2\pi r dr \qquad \text{Eq[S1-5]}$$

where $h = 2\sqrt{r_{vdW,A}^{\,2} - r^2}$ for $r_{vdW,A'} < r \le r_{vdW,A}$

$h = 2\sqrt{r_{vdW,A}^{\,2} - r^2} - 2\sqrt{r_{vdW,A'}^{\,2} - r^2}$ for $0 < r \le r_{vdW,A'}$

We obtain the dependence of $\xi_{A,x}$ on λ_x as shown in Table S1-2. For an expected $\lambda_x \sim 20$ Å for the C1s core level, $\xi_{A,x}$ is 0.66, which agrees with experiment.

λ_x (Å)	$\xi_{A,x}$
15	0.58
20	0.66
25	0.72
30	0.76

Table S1-2. Dependence of $\xi_{A,x}$ on λ_x evaluated in a continuum model.

1.3 Dependence of photoelectron transmission factor $\xi_{G,x}$ for graphene

At the same level of approximation, for graphene,

$$\xi_{G,x} = exp(-\frac{h}{\lambda_x}) \qquad \text{Eq[S1-6]}$$

where h = 3.35 Å.

We obtain the dependence of $\xi_{G,x}$ on λ_x as shown in Table S1-3. Experimentally however, $\xi_{G,C1s}$ is considerably smaller, at 0.45 ±0.03. For HOPG, $\lambda \sim 15$ Å. Hence a single sheet of (suspended) graphene is far more effective in attenuating elastic photoemission than HOPG, or what bulk λ predicts. This is further confirmed by the strong attenuation of the substrate photoemission (Si2p from SiO_2) with each additional G layer in the assembly. This suggests the presence of other mechanisms that can strongly attenuate photoelectron transmission through graphene, which we postulate to be surface plasmon excitations. Such a mechanism would not apply to $C_{60}F_{48}$.

λ_x (Å)	$\xi_{G,x}$
15	0.80
20	0.85
25	0.87
30	0.98

Table S1-3. Dependence of $\xi_{G,x}$ on λ_x evaluated in a continuum model.

1.4 Dependence of self-transmission factor $\eta_{A,x}$ for $C_{60}F_{48}$

The self-transmission of $C_{60}F_{48}$ is determined by the thickness of material through which the emitted photoelectron passes. For photoemission from the C1s core in the C_{60} cage with r_{C60}, this is given in the continuum approximation by,

$$\eta_{A,x} = \int_0^{\pi} exp(-\frac{h}{\lambda_x}) 2\pi {R_{C60}}^2 sin\theta d\theta \Big/ \int_0^{\pi} 2\pi {R_{C60}}^2 sin\theta d\theta \qquad \text{Eq[S1-6]}$$

where $h = \sqrt{{r_{vdW,A}}^2 - r^2} - \sqrt{{r_{C60}}^2 - r^2}$ for $0 < \theta \leq \frac{\pi}{2}$

$h = \sqrt{{r_{C60}}^2 - r^2} + \sqrt{{r_{vdW,A}}^2 - r^2}$ for $\frac{\pi}{2} < \theta \leq \frac{\pi}{2} + cos^{-1}(\frac{r_{vdW'}}{r_{C60}})$

$h = \sqrt{{r_{C60}}^2 - r^2} + \sqrt{{r_{vdW,A}}^2 - r^2} - 2\sqrt{{r_{vdW,A'}}^2 - r^2}$

for $\frac{\pi}{2} + cos^{-1}(\frac{r_{vdW'}}{r_{C60}}) < \theta \leq \pi$

We obtain the dependence of $\eta_{A,x}$ on λ_x as shown in Table S1-4. The results suggest that photoemission for $C_{60}F_{48}$ is significantly self-attenuated. Small uncertainties in $r_{vdW,A}$, r_{C60} and $r_{vdW,A'}$ do not change the results much.

λ_x (Å)	$\eta_{A,x}$
15	0.70
20	0.76
25	0.80
30	0.83

Table S1-4. Dependence of $\eta_{A,x}$ on λ_x evaluated in a continuum model.

1.5 Dependence of self-transmission factor $\eta_{G,x}$ for graphene

At the same level of approximation, the self-transmission of graphene is given by,

$$\eta_{G,x} = exp(-\frac{h}{\lambda_x}) \qquad \text{Eq[S1-7]}$$

where the half-thickness of graphene h = 1.7 Å

We obtain the dependence of $\eta_{G,x}$ on λ_x and $\eta_{A,x}$ / $\eta_{G,x}$, as shown in Table S1-5. The results show that the relative "visibility" of $C_{60}F_{48}$ relative to graphene is significantly below unity. For an expected $\lambda \sim 20$ Å, $\eta_{A,x}$ / $\eta_{G,x}$ is 0.83, which agrees with experiment.

λ_x (Å)	$\eta_{G,x}$	$\eta_{A,x}$ / $\eta_{G,x}$
15	0.89	0.78
20	0.92	0.83
25	0.93	0.86
30	0.94	0.88

Table S1-5. Dependence of $\eta_{G,x}$ on λ_x evaluated in a continuum model, and the ratio $\eta_{A,x}$ / $\eta_{G,x}$ obtained by combining with data from Table S1-4.

Supplementary Information 2

Evaluation of polarization energies and ion–ion interaction energies at the surface and in the interior of graphene/ dopant assemblies

2.1 Non-polarizable dopant ion model

Ion on graphene surface. The polarization energy (u_{pol}) for a charged ionized dopant located above the surface of graphene due to interaction with hole carrier in the graphene sheet corresponds in the limit of perfect screening to the well-known case of an ion located above a grounded perfectly-conducting sheet. In this limit, u_{pol} is given by,

$$u_{pol} = -\frac{1}{8\pi\varepsilon_o r_o}\frac{q^2}{}\left(1-\frac{1}{\varepsilon_r}\right) - \frac{1}{8\pi\varepsilon_o\varepsilon_r 2z}\frac{q^2}{} \qquad \text{Eq[S2-1]}$$

where q is the charge of dopant ion, r_o is a cut-off radius below which the assumption of point charge or continuum electrostatics breaks down, ε_o is vacuum permittivity, ε_r is the effective medium dielectric constant, and z is the distance from center of ion to mid-plane of conducting sheet, with $z > r_o$. The first term represents medium polarization effects, while the second graphene screening (polarization) effects. The dependence of u_{pol} on z for ε_r = 1.00 is shown for illustration in Supplementary Figure 4 (top panel).

Ion sandwiched between two graphene sheets. u_{pol} for a charged ionized dopant located in a symmetrical sandwich between two graphene sheets (in the interior) due to interaction with hole carrier in the bounding graphene sheets corresponds in the limit of perfect screening to the case of an ion located symmetrically between two grounded perfectly-conducting sheets. We computed the electrostatic field E by applying the well-known method of images,

$$\vec{E} = \frac{1}{4\pi\varepsilon_o\varepsilon_r}\left(\frac{q}{r^2}\hat{r} + \sum_n \frac{q_n}{r_n{}^2}\hat{r}_n\right) \qquad \text{Eq[S2-2]}$$

where q is the charge of the dopant ion, r is its distance to the field point, $\hat{r}$ is the corresponding unit vector, q_n is an image charge, r_n is its distance to the field point, $\hat{r}_n$ is the

corresponding unit vector, and the index $n \in$ even gives the number of images (each pair symmetrically disposed). The summation over image charges oscillates with n. A trick was used to truncate the calculations efficiently. The last image on each side was assigned a charge value that is half of the actual image value to preserve system charge neutrality. The sum was then recomputed for n+2 images by adding one more image to each side, and the two results averaged.

The electrostatic field energy u'_{el} was then computed using,

$$u'_{el} = \int_{V'} \frac{1}{2} \varepsilon_o \varepsilon_r E^2 dV' \qquad \text{Eq[S2-3]}$$

where V' is the volume bounded by the conducting sheets less the excluded volume of the dopant ion corresponding to a radius r_S. The electrostatic field energy u_{el} for the free ion in vacuum, which is the final state of the DFT calculations, is given by,

$$u_{el} = \int_{V} \frac{1}{2} \varepsilon_o \varepsilon_r E^2 dV \qquad \text{Eq[S2-4]}$$

where E here is the standard electrostatic field of the point charge, $\varepsilon_r = 1$ for $r \geq r_{vdW,A}$ but ε_r for $r_S \leq r < r_{vdW,A}$, and V is the entire volume in space less the excluded volume of the dopant ion. This gives,

$$u_{el} = (7.199 \text{ eV Å}) \left(\frac{(q/e)^2}{r_{vdW,A}} + \frac{(q/e)^2}{\varepsilon_r} \left(\frac{1}{r_S} - \frac{1}{r_{vdW,A}} \right) \right) \qquad \text{Eq[S2-5]}$$

u_{pol} was then computed as the difference,

$$u_{pol} = u'_{el} - u_{el} \qquad \text{Eq[S2-6]}$$

The dependence of u_{pol} on z for $\varepsilon_r = 1.00$ is shown for illustration in Supplementary Figure 4 (bottom panel). The excluded volume used corresponds to a cut-off radius of 2.45 Å, but the results are not sensitive to uncertainties in this value.

2.2 Perfectly-conducting dopant ion sphere model

Ion on graphene surface. The polarization energy (u_{pol}) for a charged ionized dopant modeled as a perfectly-conducting sphere located above the surface of graphene due to interaction with hole carrier in the graphene sheet corresponds in the limit of perfect screening to the case of a perfectly-conducting sphere with fixed charge located above a grounded perfectly-conducting sheet. We computed the electrostatic field E by applying the well-known method of images, then Eqs[S2-2]–[S2-6] to find u_{pol}. The excluded volume for the integration r_S is now clearly identified as the radius of the conducting sphere, which is slightly larger than r_{C60} due to charge delocalization onto C-F bonds (Figure 2e, main paper).

Ion sandwiched between two graphene sheets. Similarly u_{pol} for a charged ionized dopant modeled as a perfectly-conducting sphere in the interior of the graphene assembly interacting with hole carriers in the graphene sheet corresponds in the limit of perfect screening to the case of a perfectly-conducting sphere with fixed charge in a symmetrical sandwich between two grounded perfectly-conducting sheets. We thus computed the electrostatic field E as above by applying the well-known method of images, then Eqs[S2-2]–[S2-6] to find u_{pol}. We show the dependence of u_{pol} on ε_r and r_S in Table S2-1.

ε_r	u_{pol} (eV)	
	r_S = 3.75 Å	r_S = 4.75 Å
1.00	−0.58	−0.60
1.50	−0.76	−0.78
2.00	−0.84	−0.86
2.50	−0.89	−0.91
3.00	−0.93	−0.94

Table S2-1. Dependence of u_{pol} on ε_r and r_S for the symmetrical sandwiched configuration (distance of center of ion to mid-plane of either conducting sheet, z = 8.3 Å) evaluated by classical electrostatics.

The results for ε_r compared with the non-polarizable ion model (Supplementary Figure 4, bottom panel) for the graphene/ $C_{60}F_{48}$ assembly show that polarization correction due to screening by the electron on $C_{60}F_{48}^-$ is small for the dimensions of the system, < 0.05 eV. A larger correction comes from ε_r effects. For $\varepsilon_r \approx 2.5$, $u_{pol} \approx -0.9$ eV.

Although graphene is not a perfect conductor, a single sheet of graphene is sufficient to practically screen much of the dc electric field. Hence these calculations conducted in the classical electrostatic limit is sufficiently accurate for our purpose of estimating acceptor level energy to ±0.1 eV or so.

2.3 Ion–ion Coulomb interaction energy

The ion–ion interaction energy u_{el} for a 2D array of ions bound on one side or both sides by perfectly conducting sheets is computed in the point charge approximation using the method of images. The electrostatic potential contributions from all other ions and their images were summed,

$$u_{el} = \frac{1}{2} \frac{q_o}{4\pi\varepsilon_o\varepsilon_r} \sum_i \left(\frac{q_i}{r_i} + \sum_n \frac{q_{in}}{r_n} \right) \qquad \text{Eq[S2-7]}$$

where q_i is the charge of an ion (other than but otherwise identical to the test ion q_o), r_i is its distance to the test ion, index *i* runs over all the ions, q_{in} is an image charge of the ion, r_{in} is its distance to the test ion, and index *n* runs over all images of the ion, where $\frac{1}{2}$ corrects for double counting of the electrostatic potential energy terms in the energy sum for each ion.

We used a hexagonal 2D lattice array for ion positions. We found that the finite sum due to ions included in a radius of about ten times of the lattice constant (given by the nearest ion–ion distance *a*) is sufficient to closely approach the infinite array. Because large lattice constants relative to the distance of ion to conducting sheet *z* are of interest, a large number of images had to be included. In our calculations, we used 1,000 images. The trick described in Supplementary Information 2.1 to perform accurate truncation of infinite image sums were employed. We used ε_r = 1.00 to generate the plots of u_{el} as a function of *a* and *z* shown in Supplementary Figure 5.