Supporting Information

Electrografted Fluorinated Organic Ultrathin Film as Efficient Gate Dielectric in MoS_2 Transistors

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Chemical synthesis of the diazonium compound. All reagents and chemicals were purchased from Aldrich and were used as received. NMR spectra were recorded with a Bruker ADVANCE DRX 400 (400 MHz). Chemical shifts δ are expressed in ppm relative to tetramethylsilane (TMS). Infrared spectroscopy (IR) was realized with a Bruker Vertex 70 spectrometer (resolution 2 cm^{-1}, 24 scans collected, MCT detector) equipped with a Pike Miracle plate for ATR.

The 4-heptadecafluorooctylbenzene diazonium tetrafluoroborate ($C_8F_{17}BD$) was synthesized according to the procedure depicted in Figure S1. Under argon, nitrosium tetrafluoroborate salt (301 mg, 1.2 eq.) was added directly to a degassed solution at -40°C of 4-heptadecafluorooctylaniline (1.1 g, 2.15 mmol) dissolved in dry acetonitrile (4 mL). After 15 min of stirring at this temperature, diethyl ether was added until a precipitate came out. The precipitate was filtrated, washed several times with diethyl ether to give a white powder of 4-heptadecafluorooctylbenzene diazonium tetrafluoroborate $C_8F_{17}BD$ (1.02 g, yield 78 %). δ ^1H NMR (400 MHz; CD_3CN): 7.73 (2H, m), 8.42 (2H, m). ν_{max}/cm^{-1}: 2308 ($\nu_{N=N}$).

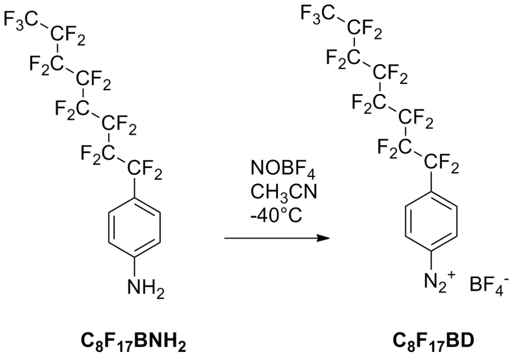

Figure S1. Synthesis pathway of 4-heptadecafluoro-octyl-benzene-diazonium tetrafluoroborate bearing one diazonium salt function.

Electrochemical grafting of $C_8F_{17}BD$ compound on patterned gold electrodes. The electrochemical grafting was conducted in a single-compartment, three-electrode cell in a glovebox with a Bio-Logic potentiostat (Model VSP). $Ag/AgNO_3$ (10 mM) electrode and a platinum wire served as reference and counter electrode, respectively. All potentials are referenced to $Ag/AgNO_3$. The silicon substrate with the patterned gold working electrodes was completely immersed in a solution of $C_8F_{17}BD$ (10^{-3} M) dissolved in tetrabutylammonium hexafluorophosphate (10^{-1} M)/Acetonitrile electrolyte. The gold electrodes were connected with a passivated tungsten tip. Cyclic voltammetry technique (5 scans at 20 mV/s; Figure S2) was used to make smooth thin layer film of C_8F_{17}BD on patterned gold electrodes.

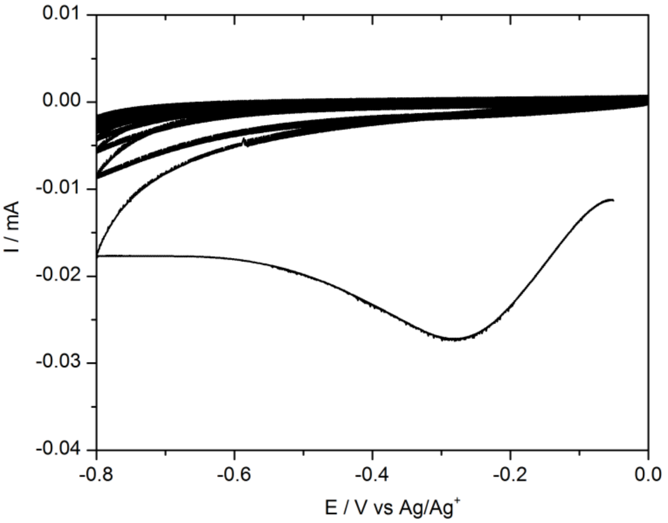

Figure S2. Voltammetric reduction of C_8F_{17}BD (10^{-3} M) with tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte in CH_3CN on gold electrodes, scan rate 20 mV.s^{-1}.

XPS measurements on gold wafer electromodified by C_8F_{17}BD. Gold-coated silicon wafers (<111> oriented, 1000 Å coating, titanium adhesion layer, 4 in. x 500 μm) for XPS analysis were purchased from Sigma Aldrich. X-ray photoemission spectroscopy (XPS) analyses were performed with a Kratos Axis Ultra DLD using a high-resolution monochromatic Al-Kα line X-ray source at 1486.6 eV. Fixed analyser pass energy of 20 eV was used for core level scans. Survey spectra were captured at pass energy of 160 eV. All spectra were referenced with an external gold substrate with a binding energy of 84.0 eV for Au 4f.

XPS analyses of the electrografted film show clearly the peaks of carbon and fluorine, and gold (Figure S3, top left) in agreement with the chemical structure of the diazonium compound (No nitrogen is detected since diazonium function were removed during the electrochemical reduction) and the substrate, respectively. Analysis of the C1s region (Figure S3, top right) shows three peaks with a bonding energy at 293.7 eV, 291.6 eV and 285.3 eV corresponding to carbon from CF_2 groups, CF_3 groups and from the aromatic rings, respectively. Fitting and integration of the different peaks show a ratio of 1:7:6 in agreement with the ratio carbon of the fluorinated chains/aromatic carbons (8/6).

The expanded F1s region shows one peak (Figure S3, bottom right) centered at 689.0 eV. Moreover, it is worth noting that there are no nitrogen or phosphorus atoms in the film. It shows that the electrolyte is not trapped during the film electrografting. Hence, the electrodeposited film is composed of fluorinated aliphatic chains and aromatic rings.

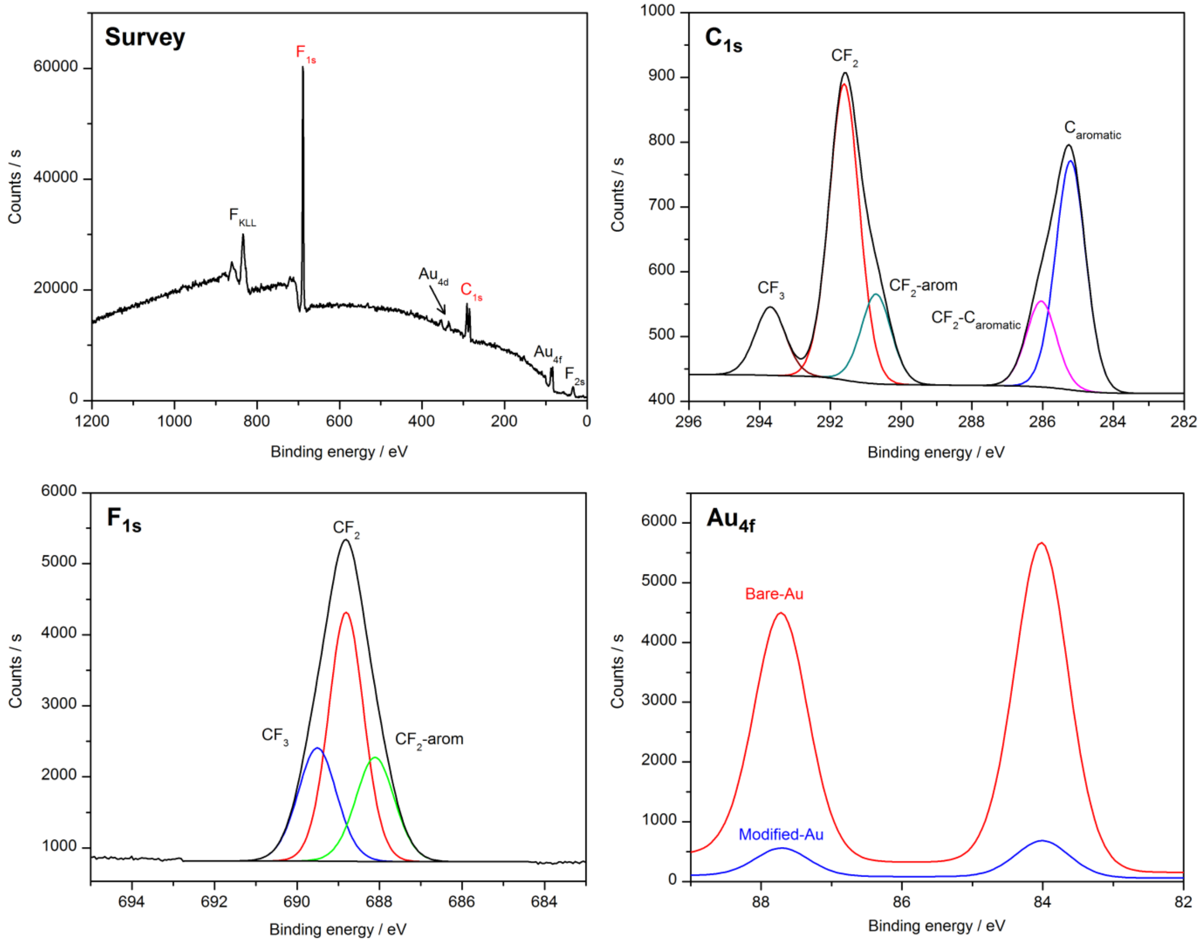

Figure S3. XPS survey (top right), C1s (top left), F1s (bottom right) spectra of $C_8F_{17}BD$ electrografted on gold coated silicon wafer. XPS measurement of Gold attenuation signal (bottom left), bare electrode (red) and modified gold electrode (blue).

The gold signal attenuation (Figure S3, bottom right), observed after the electroreduction step, is due to the covering of the electrode by the organic layer. This attenuation can be used to provide an estimation of the organic layer thickness. Indeed, the relative inhibition of the Au $4f_{7/2}$ signal can be expressed as: $I/I_0 = \exp(-d/\lambda \sin \theta)$ where d is the layer thickness, λ the mean free path of the substrate-specific photoelectron in the organic layer, θ the analysis takeoff angle relative to the surface, and I/I_0 the ratio of the Au $4f_{7/2}$ peak intensities (modified surface/bare surface).

In the experiments, the takeoff angle was 90° and the value of λ was deduced from the empirical formula derived by Seah and Dench [1]: $\lambda_k = A_n/E_k + B_nE_k^{1/2}$ where E_k is the kinetic energy of photoelectrons. For an Al Kα source $E_k = 1486.6 - EB$.

If the substrate is coated with organic materials, $A_n = 49$ and $B_n = 0.11$, here the unit of λ is $mg.m^{-2}$ and the unit of energy is the eV. To convert λ into nanometer units, one has to divide λ in $mg.m^{-2}$ by the density of the layers, assumed here to be to 1.015 g/cm^3 as an aniline derivatives layer. Using these parameters and based on the Au $4f_{7/2}$ peak, λ_k is calculated to be 4.09 $mg.m^{-2}$ and the aryl layer thickness is found to be around 8.0 nm.

Electrografted gold electrodes used as gates in MoS_2 FETs

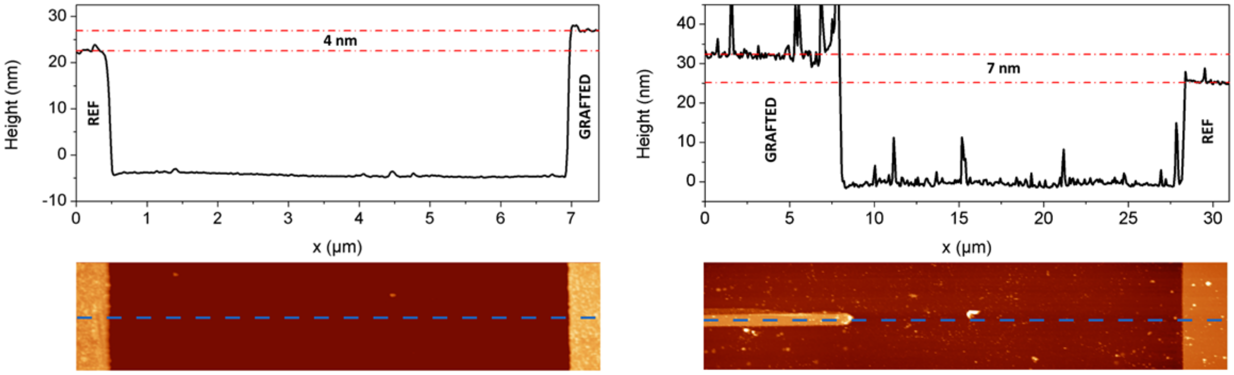

Figure S4. AFM images and height profiles of 4 nm thick (left) and 7 nm thick (right) organic films electrografted on gold electrodes. On each image, a gold electrode was not electrografted and serves as a reference.

Estimation of the permittivity of the organic dielectric (C_8F_{17}BD). The permittivity of the organic dielectric was estimated from the subthreshold slopes of the transfer characteristics depicted in Figure 3a. Indeed, knowing the thickness ratio between the two dielectrics involved (SiO_2 -150 nm- and C_8F_{17}BD -7nm-), we can estimate the permittivity ratio, as detailed below.

The subthreshold can be expressed as: $S = \frac{k \times T}{q} \times \ln(10) \times (1 + \frac{C_D \times C_{IT}}{C_{diel}})$,

where k is the Boltzmann constant, T is the temperature, q is the electron charge, C_D is the depletion capacitance, C_{IT} is the capacitance associated with interface traps and $C_{diel} = \frac{\varepsilon_0 \times \varepsilon_{diel}}{t_{diel}}$ is the capacitance of the gate dielectric (where ε_0 is the vacuum permittivity, ε_{diel} is the relative dielectric permittivity and t_{diel} is the dielectric thickness).

With $K = \frac{k \times T}{q} \times \ln(10) = 60\ mV$, we obtain: $S_{SiO_2} = K \times (1 + \frac{C_D + C_{IT}}{C_{SiO_2}})$ and

$S_{orga} = K \times (1 + \frac{C_D + C_{IT}}{C_{orga}})$. Considering that C_D dominates over C_{IT}, $S_{SiO_2} = K \times (1 + \frac{C_D}{C_{SiO_2}})$ and $S_{orga} = K \times (1 + \frac{C_D}{C_{orga}})$. It comes that: $\frac{C_{orga}}{C_{SiO_2}} = \frac{S_{SiO_2} - K}{S_{orga} - K}$ and thus: $\frac{\epsilon_{orga}}{\epsilon_{SiO_2}} = \frac{S_{SiO_2} - K}{S_{orga} - K} \times \frac{t_{orga}}{t_{SiO_2}}$

Since we measured:

$S_{SiO_2} = 1.8 \frac{V}{decade} for\ t_{SiO_2} = 150\ nm$ and $S_{orga} = 145 \frac{mV}{decade} for\ t_{orga} = 7\ nm$

We obtain: $\frac{\epsilon_{orga}}{\epsilon_{SiO_2}} \approx 1$

This means that the permittivity of the organic dielectric is close to the one of SiO_2.

References

(1) Briggs, D.; Seah, M. P. Pratical *Surface Analysis: Auger and X-Ray Photoelectron Spectroscopy*; John Wiley: Chichester, U.K., 1990.