Preparation of alkyl silane monolayers.

The Si face of an <0001> oriented SiC substrate (PAM-Xiamen (PRC)) was first cleaned by sonication in Isopropyl solution, and subjected to 3 repeated cycles of oxidation in O₂ plasma and etching in 5% HF. Then finally the substrates were cleaned with deionized water and blown dried in N₂ flow. This procedure has been shown to produce an atomically flat hydroxilated surfaces. Then the substrates were incubated in a solution of trimethoxy alkyl silane in Toluene. N,N-di-isopropylethylamine was used as catalyst in the reaction and the temperature of the reaction bath was maintained at 65-70° C. This reaction is sensitive to moisture content on SiC surface and Toluene. To minimize the
sensitivity, toluene is dried over molecular sleeves and the reaction was carried out in a closed glass vial. The following table gives the concentration and reaction condition for the monolayer grafting.

Table S1: Molecular Monolayer grafting protocol.

<table>
<thead>
<tr>
<th>Monolayer</th>
<th>Precursor</th>
<th>Amount of precursor (μl)</th>
<th>Amount of Toluene (μl)</th>
<th>Amount of Catalyst (μl)</th>
<th>Time of incubation (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH₃</td>
<td>Trimethoxy methyl silane</td>
<td>40</td>
<td>1000</td>
<td>10</td>
<td>150</td>
</tr>
<tr>
<td>-C₂H₅</td>
<td>Trimethoxy ethyl silane</td>
<td>80</td>
<td>1000</td>
<td>10</td>
<td>150</td>
</tr>
<tr>
<td>-C₄H₉</td>
<td>Trimethoxy butyl silane</td>
<td>150</td>
<td>1000</td>
<td>10</td>
<td>150</td>
</tr>
<tr>
<td>-C₈H₁₇</td>
<td>Trimethoxy octyl silane</td>
<td>220</td>
<td>1000</td>
<td>10</td>
<td>150</td>
</tr>
</tbody>
</table>

After completion of the reaction, all the samples were sonicated for 5 minutes with toluene followed by another round of sonication with isopropyl alcohol for 5 minutes. Then the samples were rinsed with isopropyl alcohol and blow dried in a dry N₂ flow.
Figure S1: UPS spectrum of Pentacene thin films (of different thicknesses) deposited on silane-modified SiC surface (blue line), a SiC surface with only the siloxane monolayer (black line) and
a bare SiC surface (red line). Both the low (kinetic) energy (left) and the high energy ranges are shown. The uncertainty in these numbers is 0.1eV. The corresponding energy level diagrams for C1 (a) C4(b) and C8(c) are shown in the right. It can be seen that the energy level alignment at the interfaces are same within the measurement error of UPS.
Figure S2: SEM micrographs of pentacene films on C1 (a) and C8 monolayer (b). The grain size in the film is visibly higher for the C8 than for the C1 monolayer.
Figure S3: Extinction coefficient of SiC/C4/pentacene sample, measured by ellipsometer (upper curve; left-hand scale), and its numerical Gaussian derivative (lower curve; right-hand scale). The peak at the gradient appears at 1.83 eV.
Figure S4: Current-Voltage curves for SiC-MM-Pentacene devices, measured in dark.
Figure S5: Simulation of J-V curves for an organic-based solar cell, with different degrees of disorder. Figure is adapted with permission from ref 1 (© American Physical Society 2011).

References: