SUPPORTING INFORMATION:

Probing Surface States in PbS Nanocrystal Films Using Pentacene Field Effect Transistors: Controlling Carrier Concentration and Charge Transport in Pentacene

1. Characterization of PbS NCs.

(a)

(b)

Figure S1. (a) Transmission electron micrograph of the PbS NCs used in this work. Scale bar is 100 nm. (b) Absorbance spectrum of the PbS NCs showing an excitonic peak at a wavelength of 1625 nm.

2. Deposition of NC thin film by doctor blading.

Figure S2. Schematic of the doctor-blade deposition method.
Thin layers of PbS NCs were deposited by doctor-blade coating. The NC films were prepared on pre-patterned, thermally evaporated, gold electrodes and a 300 nm SiO₂ gate dielectric. As shown in Figure S2, a glass blade is translated parallel to the substrate with a gap of 100 µm. In a typical deposition ~30 µL of a 10 mg/mL PbS NC solution in chloroform was injected into the gap. The meniscus formed between the blade and the substrate was dragged across the substrate by moving the blade with a velocity of 0.5-2 mm/s. The resulting thin layer of NC solution was allowed to dry in air.

3. Comparison of ‘dark’ and ‘illuminated’ FET measurements

![Graphs showing comparisons of dark and illuminated FET measurements for different molecules.](image-url)
Figure S3: Photoinduced charge transfer at pentacene/PbS interface: drain current-gate voltage curves in the dark and under illumination with a laser diode with 650 nm wavelength for (a) BPDT-treated PbS, (b) EDT-treated PbS, (c) DMS-treated PbS and (d) MPA-treated PbS. Drain voltage was fixed at -5 V.

The electrical measurements in Figure S3 and S4 were performed in vacuum. To illuminate pentacene/PbS FETs, a red laser diode at a light intensity of 72 mW/cm$^2$ was used. In Figure S3 a gate voltage was scanned between 40 to -40 V at a drain voltage of -5 V. In Figure S4, the drain voltage was scanned between 0 and -40 V. The difference in the threshold voltage between in the dark and under illumination varied depending on the choice of the ligands. A DMS-treated PbS FET exhibited the largest threshold voltage shift as seen in Table 2.

<table>
<thead>
<tr>
<th>Forward Sweep (V)</th>
<th>Forward Sweep (V)</th>
<th>Threshold Voltage Shift (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dark</td>
<td>Light</td>
<td></td>
</tr>
<tr>
<td>BPDT</td>
<td>7.1</td>
<td>16.2</td>
</tr>
<tr>
<td>EDT</td>
<td>7.2</td>
<td>14.4</td>
</tr>
<tr>
<td>DMS</td>
<td>12.9</td>
<td>28.9</td>
</tr>
<tr>
<td>MPA</td>
<td>4.8</td>
<td>13.2</td>
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</table>

Table I: Threshold voltage shift in a forward sweep in the dark and under illumination.

If we assume that the generation rate of electron-hole pairs in the pentacene layer is much greater than the electron trapping rate, then electron accumulation in the pentacene is reasonable. The irradiance of the light source used was 72 mW/cm$^2$. The absorption coefficient of pentacene at a wavelength 650 nm is 22500 cm$^{-1}$ (see Voz, C.; Puigdollers, J.; Martín, I.; Muñoz, D.; Orpella, A.; Vetter, M.; Alcubilla, R. Solar Energy Materials and Solar Cells 2005, 87, 567.). Since the thickness of the pentacene layer as shown in Fig. 2 is on the order of 100 nm, the power density at the PbS / pentacene interface is approximately 60% of the incident power density, giving a generation rate of $10^{16}$ to $10^{17}$ (s$^{-1}$cm$^{-2}$). Therefore the traps in the PbS layer (with a density of $10^{12}$ cm$^{-2}$) are filled in 10 µs to 100 µs. This time constant is much less than the measurement time for each point of the drain current vs. gate bias data (approximately 20 ms integration time per point). Therefore it is reasonable to assume that photogenerated electrons accumulate in the pentacene.
Figure S4: Characteristic curves at different gate voltages for an EDT-treated PbS FET in the dark and under illumination.
Figure S5: Transfer curve of control device showing transport through a PbS NC film without pentacene.
Figure S6: Transfer curve of a control device showing the effect of a thick PbS NC film on the transport through a pentacene layer deposited on top of the PbS NC film. The transistor width and length were 1 mm and 40 µm respectively.
Figure S7: Transfer curve of a control device fabricated by spin casting two layers of a 10 mg/mL solution of 5.2 nm diameter PbSe NCs at 1800 RPM for 30 seconds onto prepatterned gold electrodes on a 300 nm gate oxide. The film was treated with a 0.1 M solution of EDT in acetonitrile for 5 minutes and rinsed with acetonitrile and hexane after each layer deposition. The film thickness is estimated to be greater than 50 nm. Hole mobility calculated in the linear region is 0.001 cm²/Vs. The source-drain bias was 5 V, the transistor width was 0.3 cm and length was 50 µm.