Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Engineering the optoelectronic properties of MoS_2 photodetectors through reversible noncovalent functionalization

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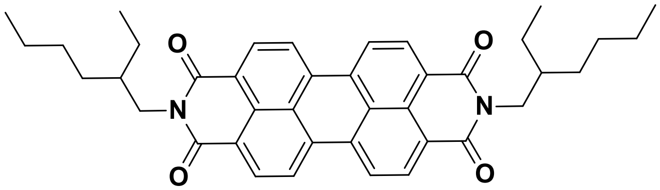
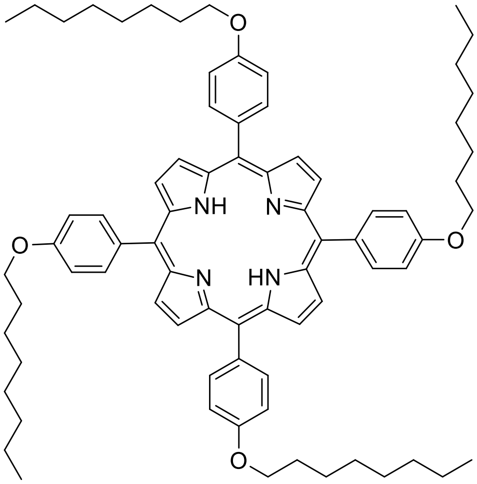
Synthesis and characterization of perylenediimide (PDI) and tetraphenyl porphyrin (TPP)



The **N,N´-bis(2-ethylhexan-1-amine)perylene-3,4,9,10-tetracarboxylic dianhydride** was synthesized and characterized as describe in *J. Org. Chem.* **2015**, *80*, 3036-3049, and showed identical spectroscopic data to those reported therein.



5,10,15,20-tetra-(4-octyloxyphenyl)porphyrin. 5,10,15,20-tetra-(4-hydroxyphenyl)porphyrin (500 mg, 0.74 mmol) was dissolved in dry DMF (100 mL) under argon and K_2CO_3 (2.65 g, 19.16 mmol) was added. 1-bromooctane (1.27 mL, 7.37 mmol) was added dropwise and the resulting mixture was stirred under reflux overnight. The mixture was poured onto cold HCl 1N and the solid was removed by filtration and dissolved in $CHCl_3$, then washed with water. The organic phase was dried over $MgSO_4$ and the solvent was removed under vacuum, obtaining the pure product. This compound (708 mg, 85% yield) was characterized by ^{1}H, ^{13}C-NMR, MALDI-TOF.

^{1}H NMR (400 MHz, $CDCl_3$) δ-2.68 (s, 2H), 0.97 (t, *J* = 6.9 Hz, 12H), 1.38 - 1.55 (m, 32H), 1.66 (q, *J* = 7.6 Hz, 8H), 2.01 (q, *J* = 6.8 Hz, 8H), 4.28 (t, *J* = 6.5 Hz, 8H), 7.30 (d, *J* = 8.8 Hz, 8H), 8.13 (d, *J* = 8.8 Hz, 8H), 8.89 (s, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 14.2, 22.8, 26.3, 29.4, 29.5, 31.9, 68.3, 112.7, 119.9, 134.5, 135.6, 158.9.

MS m/z: calculated for $C_{76}H_{94}N_4O_4$ 1127.6, found MALDI 1127.7.

Field-effect characteristics of the functionalized MoS_2-based devices

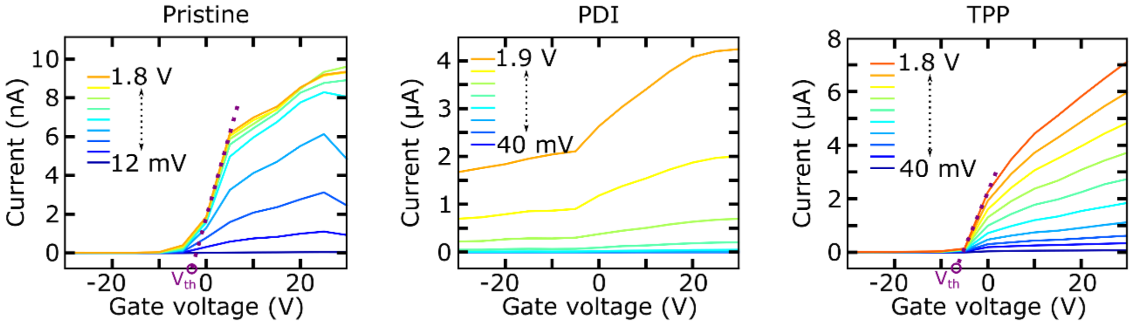


Figure S1 Current-gate voltage traces for different drain-source voltages of the device shown in the main text measured in the pristine device, the PDI-coated device and the TPP-coated device.

The current-gate voltage traces are measured in air and in dark conditions. The ON/OFF ratio in the pristine device is 400, with a mobility of $3.4 \cdot 10^{-3}$ $cm^2/V \cdot s$ and a threshold voltage of ~ -3 V. When the device is coated with PDI, the ON/OFF ratio decreases approximately a factor of 100, the mobility increases a factor of 1000 and the threshold voltage shifts below -30 V, clearly showing a high n-doping due to the presence of the molecules. When the device is coated with TPP, the ON/OFF ratio remains the same, the mobility increases a factor of 1000 and the threshold voltage shifts to ~ -8 V, indicating a moderate n-type doping. Thus for TPP we attribute the current enhancement to be dominated by a reduction of the Schottky barrier height induced by the molecule/MoS_2 charge transfer rather than the direct n-type doping.

Table S1. Field-effect characteristics of the MoS_2-based devices

	Mobility ($cm^2/V \cdot s$)	V_{th} (V)	ON/OFF ratio
Pristine	$3.4 \cdot 10^{-3}$	-3	460
PDI	0.3	< - 30	10
Cleaned	$0.5 \cdot 10^{-3}$	0	30
PDI	1.11	< - 30	10
Cleaned	$0.3 \cdot 10^{-3}$	-2	20
PDI	-	-	-
Cleaned	-	-	-
TPP	-	-	-
Cleaned	$6.6 \cdot 10^{-3}$	0	1200
TPP	1.1	-8	400
Cleaned	-	-	-
TPP	0.6	-10	10
Cleaned	$7.4 \cdot 10^{-3}$	0	2200

Table S1 Field effect characteristics of the device shown in the main text at the different cycles of coating-cleaning-functionalization.

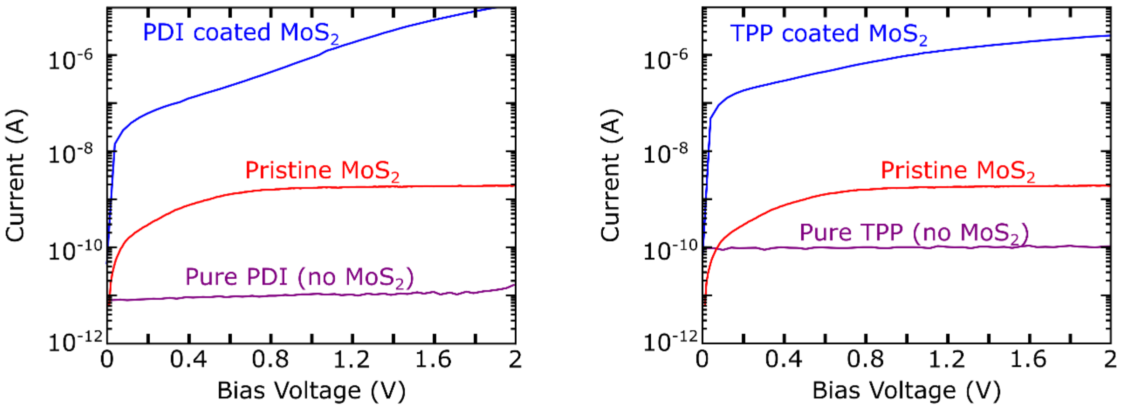


Figure S2 Comparison of the current-voltage curves measured in the pristine device, the coated device and the molecules without MoS_2 bridging the electrodes. It can be seen that the molecules are highly resistive when compared to the coated device.

UV-VIS spectra of PDI and TPP

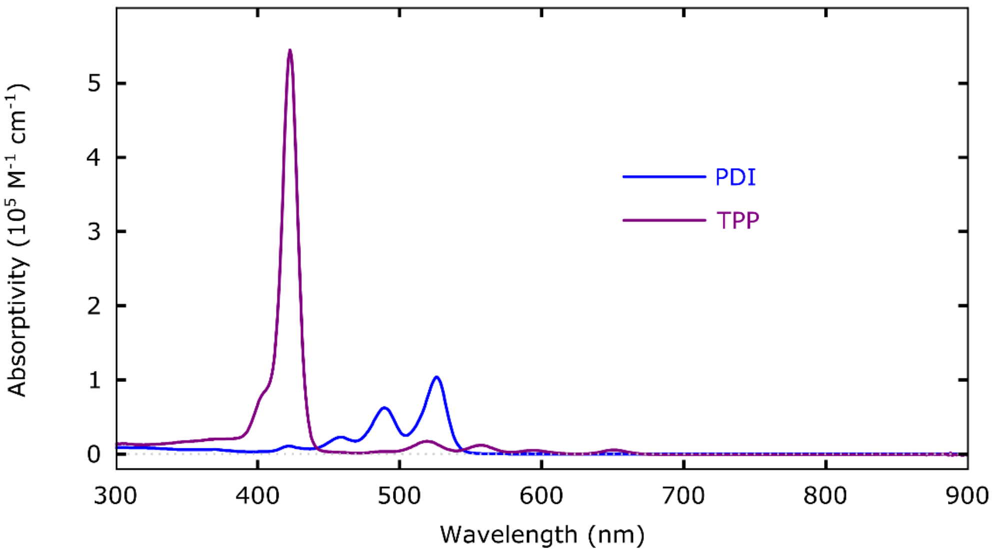


Figure S3 UV-VIS absorptivity spectra of PDI and TPP molecules in CH_2Cl_2 solution.

Optoelectronic characteristics of the functionalized MoS_2-based devices

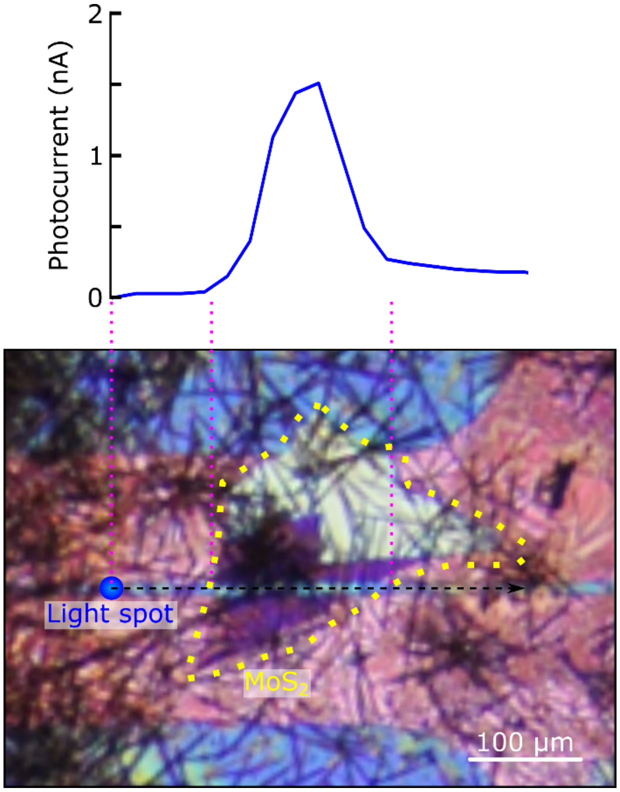


Figure S4 Scanning photocurrent of the PDI-coated device with light wavelength of 455 nm. The light spot (diameter of 25 μm) is displaced over the sample while the current between the source and drain electrodes is measured. As it can be seen, when the light spot is outside the MoS_2 flake there is not photocurrent generation.

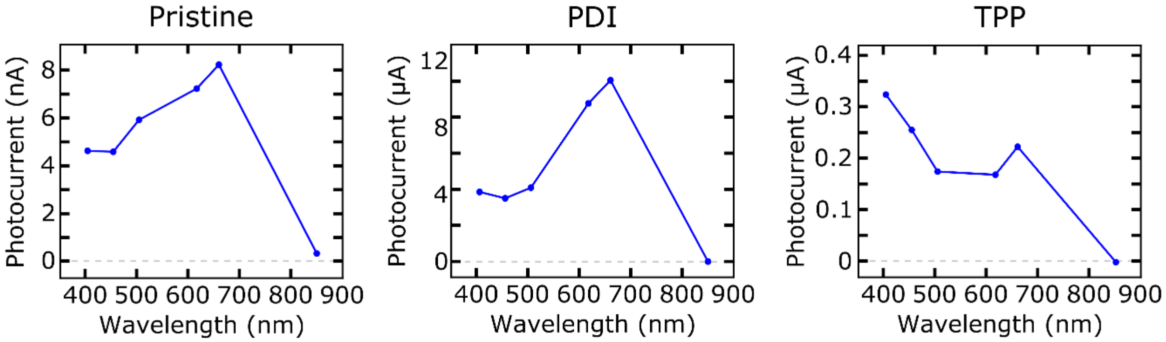


Figure S5 Photocurrent measured in the device shown in the main text as a function of the light wavelength for the pristine device, the TPP-coated device and the PDI-coated device. The LED power is 100 nW and the photocurrent is measured with $V_{ds} = 2$ V and $V_g = 30$ V.

As it is shown in the plots, the device is responding to light for wavelengths shorter than 660 nm, where there is a photocurrent peak related to the MoS_2 A exciton. The photocurrent is enhanced in the coated device about 3 orders of magnitude with respect to the pristine device, although in the

TPP-coated device the spectrum seems to be on top of a background which could be due to a high absorption of the TPP at high energies.

Differential reflectance of functionalized MoS_2

In Figure S6 we show optical microscopy and atomic force microscopy (AFM) topographic images of a monolayer MoS_2 flake transferred onto a glass substrate before and after functionalization. As can be seen in the AFM profile, the thickness of the pristine MoS_2 flake changes from 0.7 nm (monolayer) to 5-36 nm in the functionalized material due to the presence of a thin layer of TPPs.

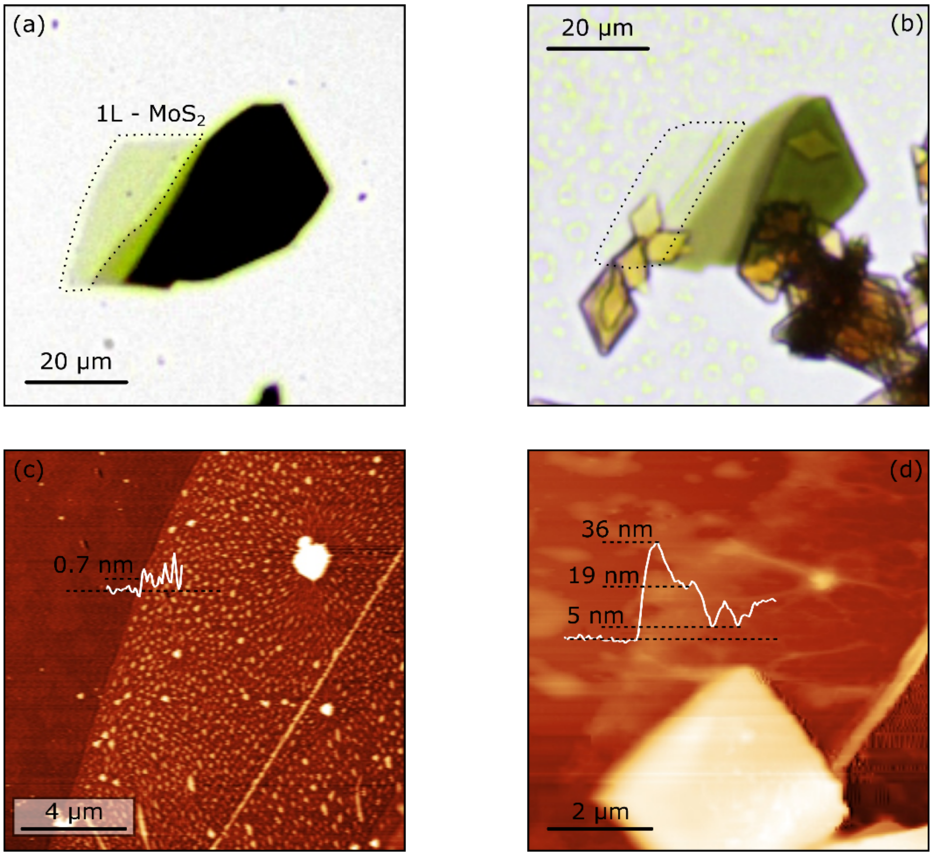


Figure S6 Optical microscopy images of **(a)** the pristine MoS_2 flake and **(b)** after functionalization with TPPs. Atomic force microscopy topographic images of **(c)** the pristine MoS_2 flake and **(d)** after functionalization reveal that MoS_2 flake is covered by a thin layer (from 5 nm to 36 nm) of TPPs.

The differential reflectance spectrum, which measures the difference in reflectance of the MoS_2 flake and the glass substrate and is related to the absorption of the material, is shown in Figure S7a for the pristine and the functionalized MoS_2. In this spectra, the two peaks at 1.89 eV ± 0.01 eV, 2.03 ± 0.01 eV are due to the generation of the A and B excitons, associated to the optical transitions at the K point of the Brillouin zone. The only appreciable change is the addition of a rather featureless background of 5-10% in differential reflectance in the TPP functionalized sample.

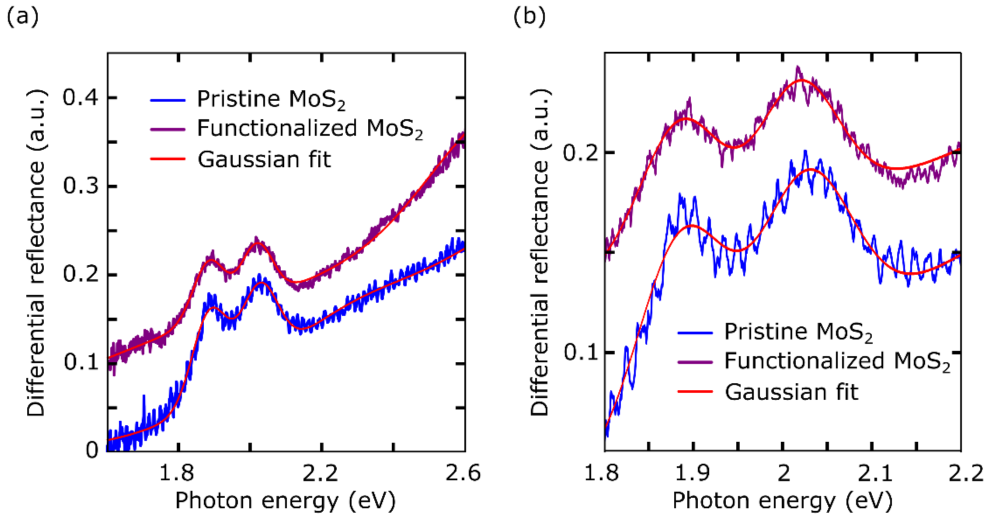


Figure S7 (a) Differential reflectance spectra of the pristine MoS_2 flake shown in Figure S6 and the functionalized flake with TPP molecules. **(b)** Gaussian fit of the main peaks appearing in (a). The fitted curves are centered at 1.89 eV ± 0.01 eV (A exciton) and 2.03 ± 0.01 eV (B exciton) in the pristine device and at 1.89 eV ± 0.01 eV and 2.02 ± 0.01 eV, respectively.