Supplementary Information for

Dye-Sensitized MoS_2 Photodetector with Enhanced Spectral Photoresponse

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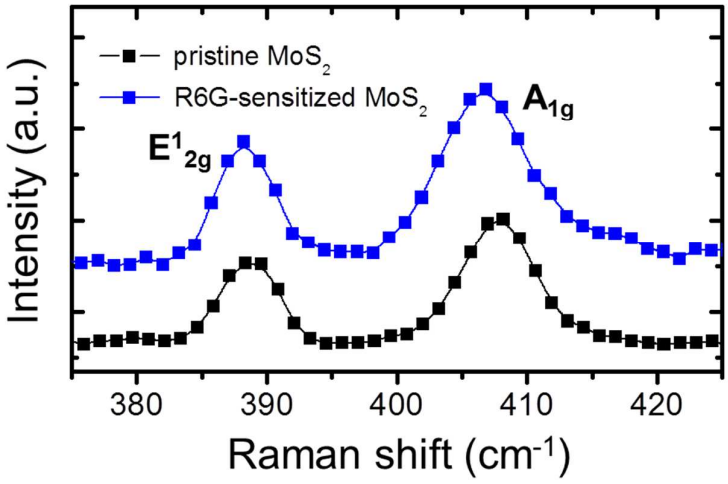

Figure S1. Raman spectra of MoS_2 single-layer before and after the deposition of R6G.

Calculation of the density of states of R6G/MoS_2 hybrid system

In order to determine the level alignment of HOMO and LUMO of R6G with respect to the molybdenum disulfide (MoS_2) monolayer energy band, we carried out a series of density functional theory (DFT) calculations. In our calculations, we assumed that there is no level mixing or charge transfer in between R6G and MoS_2 monolayer, i.e. a physisorption of R6G.

We first calculated the density of states (DOS) of unit cell of MoS_2 monolayer by employing the generalized gradient approximation (GGA) of Perdew, Burke, and Erzhenfest (PBE) functional using Vienna Ab-initio Simulation Package (VASP).[1-3] Integration over the Brillouin zone is performed on a 30 x 30 x 1 grid in the Monkhorst-Pack scheme with a plane wave basis cutoff equal to 800 eV. Although PBE often seriously underestimates the band gap of semiconducting system, for MoS_2 monolayer, we find that the band gap is computed as 1.69 eV in a reasonable agreement with the experimental value of 1.82 eV.[4] To determine the location of Fermi energy of the MoS_2 monolayer with respect to the vacuum state, we also computed the *c*-direction dependent local potential of the simulation cell (**Figure S2**), leading to the calculated work function of MoS_2 monolayer as 5.84 eV (*cf.* reported values of work function of MoS_2, ranging from 4.48 to 5.2 eV.[5, 6] For the electronic structure calculation of R6G, we then carried out all electron Gaussian type orbital (GTO) DFT calculations coupled with Pople's 6-311g**++ basis set using Jaguar module in Maestro software package [Version 9.0, Schrodinger, Inc., New York]. The optimized structure of isolated R6G are given in **Figure S3**. Calculation using PBE functional leads to the HOMO-LUMO gaps of 1.01 eV, which is ~1.4 eV underestimation compared to the experimental value of ~ 2.37 eV.[7] This is a well-known drawback of conventional GGA functionals. To fix that problem, we carried out hybrid functional DFT calculations by mixing 20% of Hartree-Fock contribution to the Hamiltonian, resulting in 2.12 eV of gap for B3LYP calculation and 2.23 eV of gap for B3PW91 calculation. We note that the structures are marginally dependent on the choice of the exchange-correlation functionals.

Based on our assumption with no level mixing or charge transfer, the MoS_2 monolayer may indirectly change the electronic structure of the R6G by inducing structural changes. To determine the structure of R6G on the MoS_2 monolayer, we further carried out PBE calculations using VASP with the semiemperical dispersion corrections (named as *ulg* correction) since the dispersion dominates the interaction between physisorbed molecule and the MoS_2.[8] Due to the relatively large simulation cell size (21.98 Å × 19.04 Å × 30.00 Å), we employed a cutoff energy of 500 eV with the 3 × 3 × 1 reciprocal space mesh. R6G is physically adsorbed on the MoS_2 monolayer, spacing between R6G and MoS_2 is 4.33 Å vs S and 5.89 vs Mo as shown in the inset of **Figure 1c**. After we determined the molecular structure of R6G as absorbed on the MoS_2 monolayer, we performed a single-point calculation to compute the HOMO-LUMO gap of this structure using B3PW91 functional which has been determined to reproduce the experimental HOMO-LUMO gap of free R6G molecule (*vide supra*). This yields the absolute location of HOMO and LUMO levels as -5.077 eV and -3.140 eV, respectively (gap is 1.937 eV; decreased from the isolated R6G of 2.23 eV).

Since the absolute locations of energy levels from all electron calculations are referenced to the vacuum level, one can align the HOMO and LUMO locations of R6G with respect to the Fermi energy of MoS_2 monolayer (which is located at -5.84 eV with respect to the vacuum level). We defined the Fermi level of the composite system of R6G and MoS_2 as

the middle of the highest level among the occupied states, which is the HOMO of R6G, and the lowest level among the unoccupied states, which is the conduction band minimum of MoS_2 as shown in **Figure 1c**.

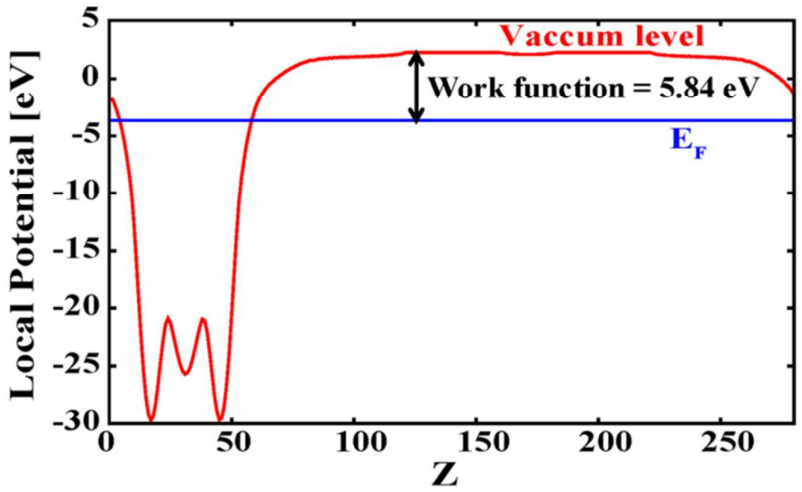

Figure S2. Local potential along the c-direction of the MoS_2 monolayer. This determines the location of the Fermi energy with respect to the vacuum level, i.e., the work function of the graphene as 5.84 eV.

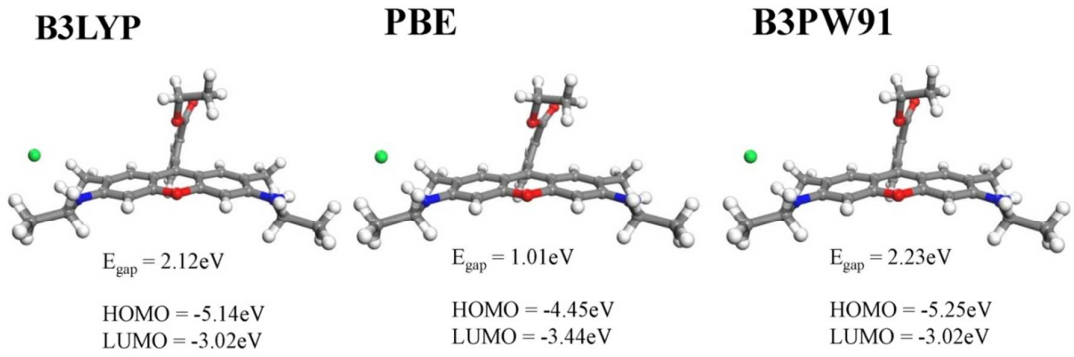

Figure S3. Optimized structures and HOMO-LUMO gaps of an isolated R6G. We performed the R6G optimization using B3LYP, PBE, and B3PW91 calculations with 6-311g**++ basis set. B3PW91 leads the best estimation on the HOMO-LUMO gap of the isolated R6G molecule showing the experimental absorption peak at 523 nm (= 2.37 eV).

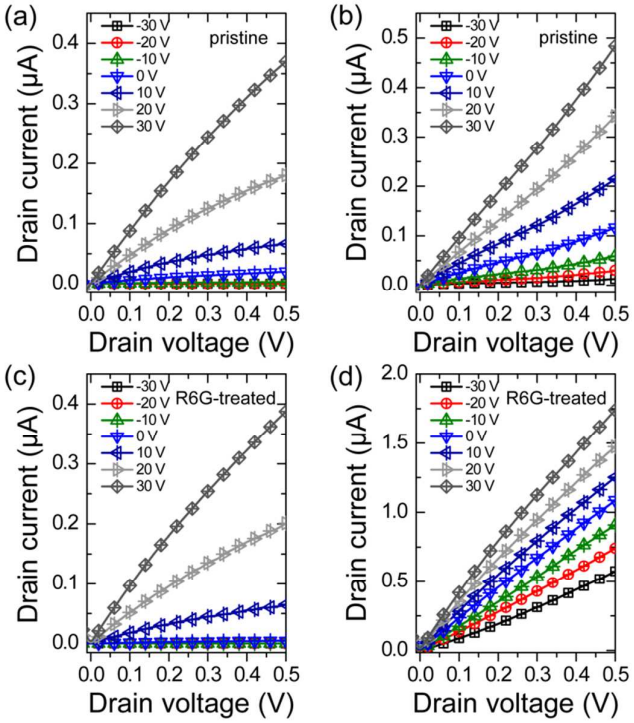

Figure S4. Photo-induced output characteristics of the pristine and R6G-sensitized MoS_2 photodetectors under (a, c) dark and (b, d) illumination (λ = 520 nm and P = 1 mW).

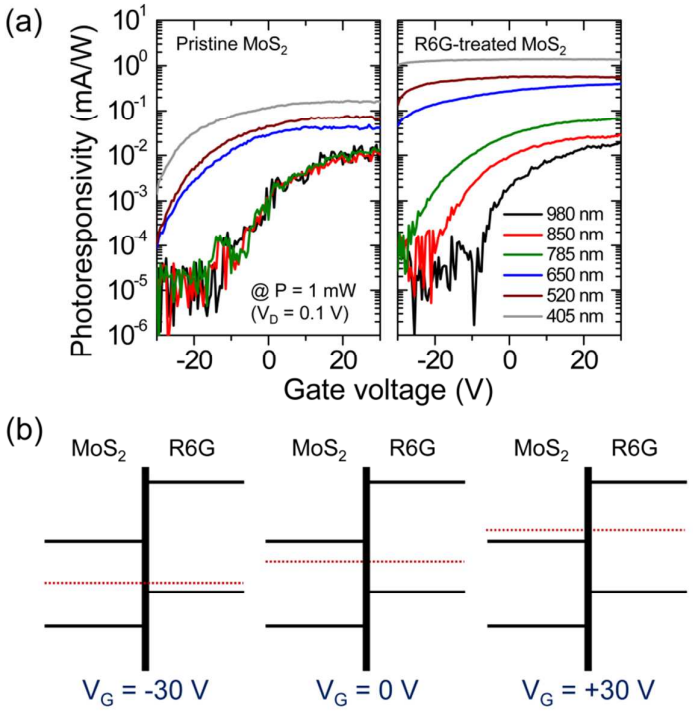

Figure S5. (a) Photocurrent as a function of the gate voltage of the pristine and R6G-sensitized MoS_2 photodetectors. (b) Schematic band structures of the R6G-sensitized MoS_2 photodetectors at different gate voltages.

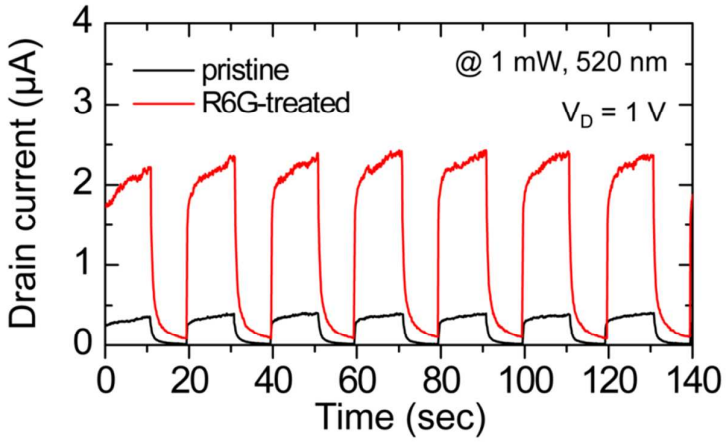

Figure S6. Photoswitching characteristics of the pristine and R6G-sensitized MoS_2 photodetectors.

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