Supporting Information

The calculation method for the Gibbs free energy difference ΔG and reorganization energy λ.

The calculation of ΔG and λ requires distinguishing between injection[1] and recombination processes[2]. First, for the case of electron injection from QD-PAHs to BP, the initial state of the electron is the LUMO state of the PbS QD-PAHs, while the final state is the LUCO+j state of BP. Therefore, the Gibbs free energy can be expressed as:

$$G_i = E_N(R_N) + E_{LUMO} - \lambda_{QD-PAHs} \tag{1}$$

$$G_f = E_N(R_N) + E_{LUCO+j} - \lambda_{BP} \tag{2}$$

In the equation, $E_N(R_N)$ represents the total energy of the lowest energy structure of the neutral system with N electrons. E_{LUMO} and E_{LUCO+j} represent the energy eigenvalues of the LUMO state of QD-PAHs and the j-th LUCO state of BP, respectively. Since both E_{LUMO} and E_{LUCO+j} are obtained from neutral structures, the neutral structure will change when they lose an electron or gain an extra electron. Therefore, it is necessary to introduce the energy change caused by structural relaxation due to electron gain or loss into the Gibbs free energy, which is the reorganization energy λ,$\lambda_{QD-PAHs}$ and λ_{BP} represent the reorganization energies of QD-PAHs and BP, respectively.

Similarly, for the case of electron recombination from BP to QD-PAHs, the initial state of the electron is the LUCO state of BP, while the final state is the HOMO state of PbS QD-PAHs. The Gibbs free energy is expressed as:

$$G_i = E_N(R_N) + E_{LUCO} - \lambda_{BP} \tag{3}$$

$$G_f = E_N(R_N) + E_{HOMO} \tag{4}$$

It is important to note that when the electron returns to the HOMO of the QD, the QD becomes a neutral structure with N electrons again. Since E_{HOMO} corresponds to the eigenvalue of the HOMO state of the neutral QD-PAHs, $\lambda_{QD-PAHs}$ does not appear in G_f

Typically, the reorganization energy λ includes the internal reorganization energy λ_i and the external reorganization energy λ_0. λ_i comes from the relaxation of the donor and acceptor structures, while λ_0 arises from the relaxation of solvent molecules and is therefore also called the solvation reorganization energy. λ_0 is generally much smaller than λ_i[3], so in our calculation model, only λ_i is considered, i.e.:

$$\lambda = \lambda_{QD-PAHs} + \lambda_{BP} \tag{5}$$

Through calculations, it was found that since 2D BP is a sufficiently large periodic system, its reorganization energy is close to 0, and λ is primarily contributed by λQD-PAHs. The reorganization energy for the electron injection process λ_{et} and the reorganization energy for the electron recombination process λ_{re} are calculated using the following formulas:

$$\lambda_{et} = E_{N-1}(R_N) - E_{N-1}(R_{N-1}) \tag{6}$$

$$\lambda_{re} = E_N(R_{N-1}) - E_N(R_N) \tag{7}$$

Where R_{N-1} and R_N represent the fixed structures of the cationic and neutral QD-PAHs, respectively. $E_N(R)$and $E_{N-1}(R)$ epresent the total energies of the neutral QD-PAHs with N electrons and the cationic QD-PAHs with N−1 electrons, respectively, for the structure R.Referring to equations (1)-(7), the numerator of the exponential term in the Marcus formula can be expressed as:

$$\Delta G + \lambda_{et} = E_{LUCO+j} - E_{LUMO} + 2\lambda_{QD-PAHs} \tag{8}$$

$$\Delta G + \lambda_{re} = E_{HOMO} - E_{LUCO} + \lambda_{QD-PAHs} \tag{9}$$

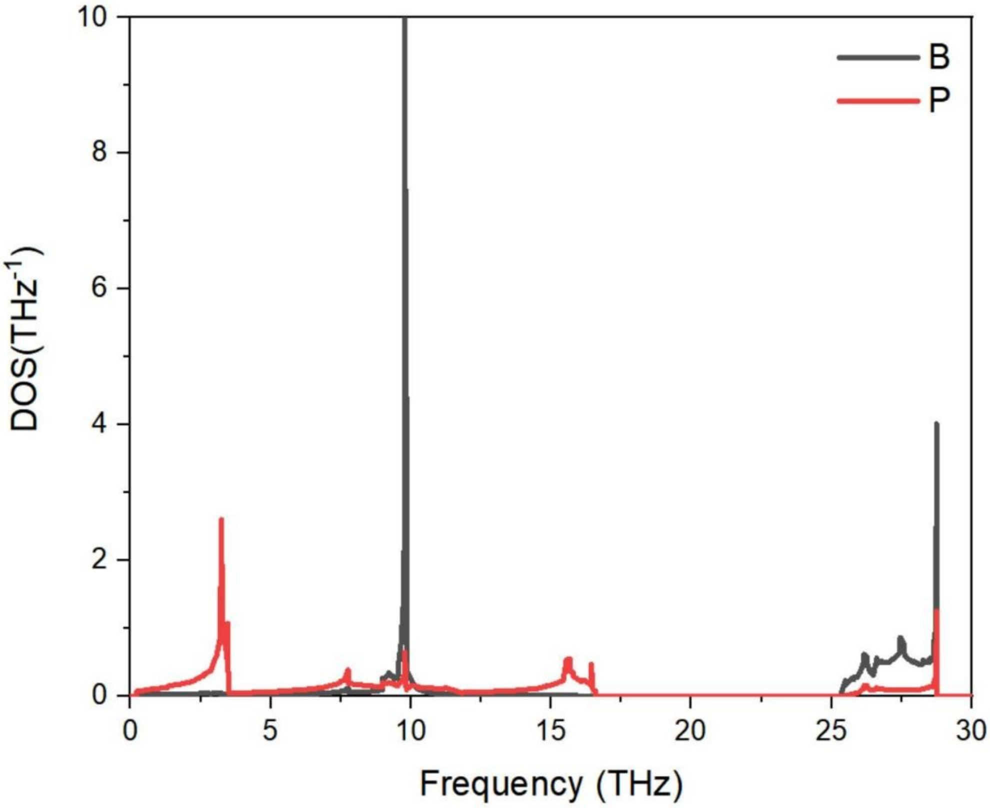

Figure S1. Projected phonon density of states of monolayer BP.

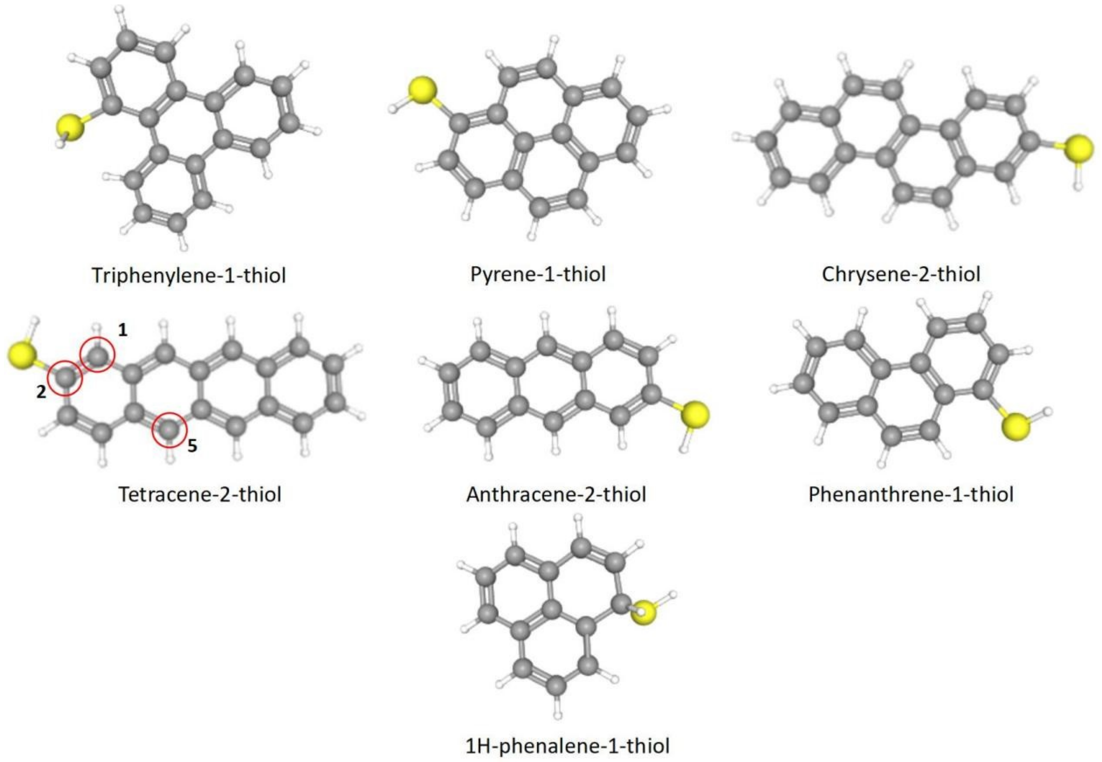

Figure S2. Schematic diagram of molecular structures, with red circles indicating different substitution sites.

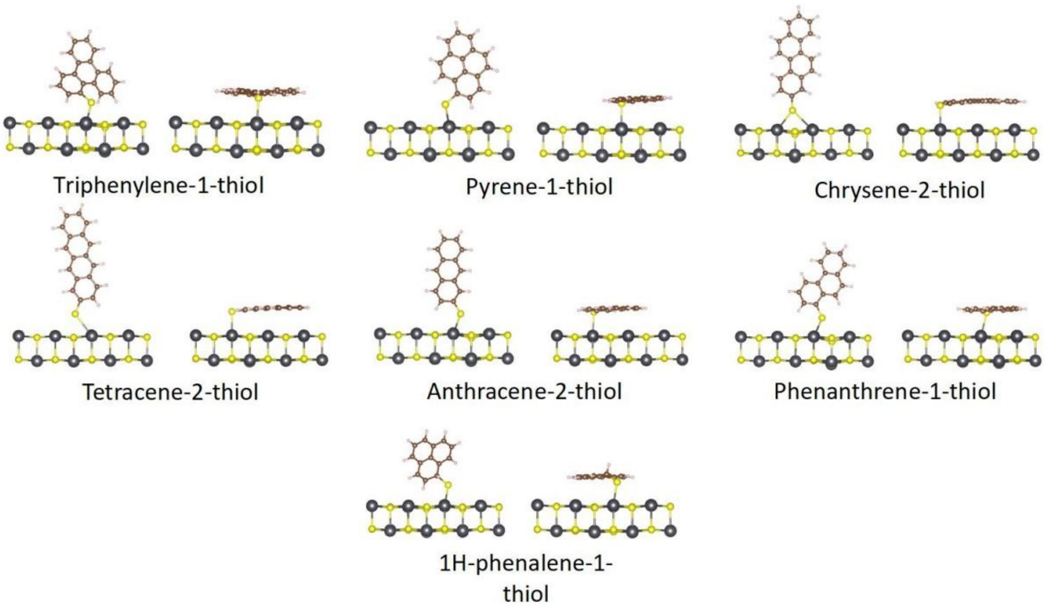

Figure S3. Relaxed structures of molecules oriented perpendicular and parallel to the PbS(100) facet.

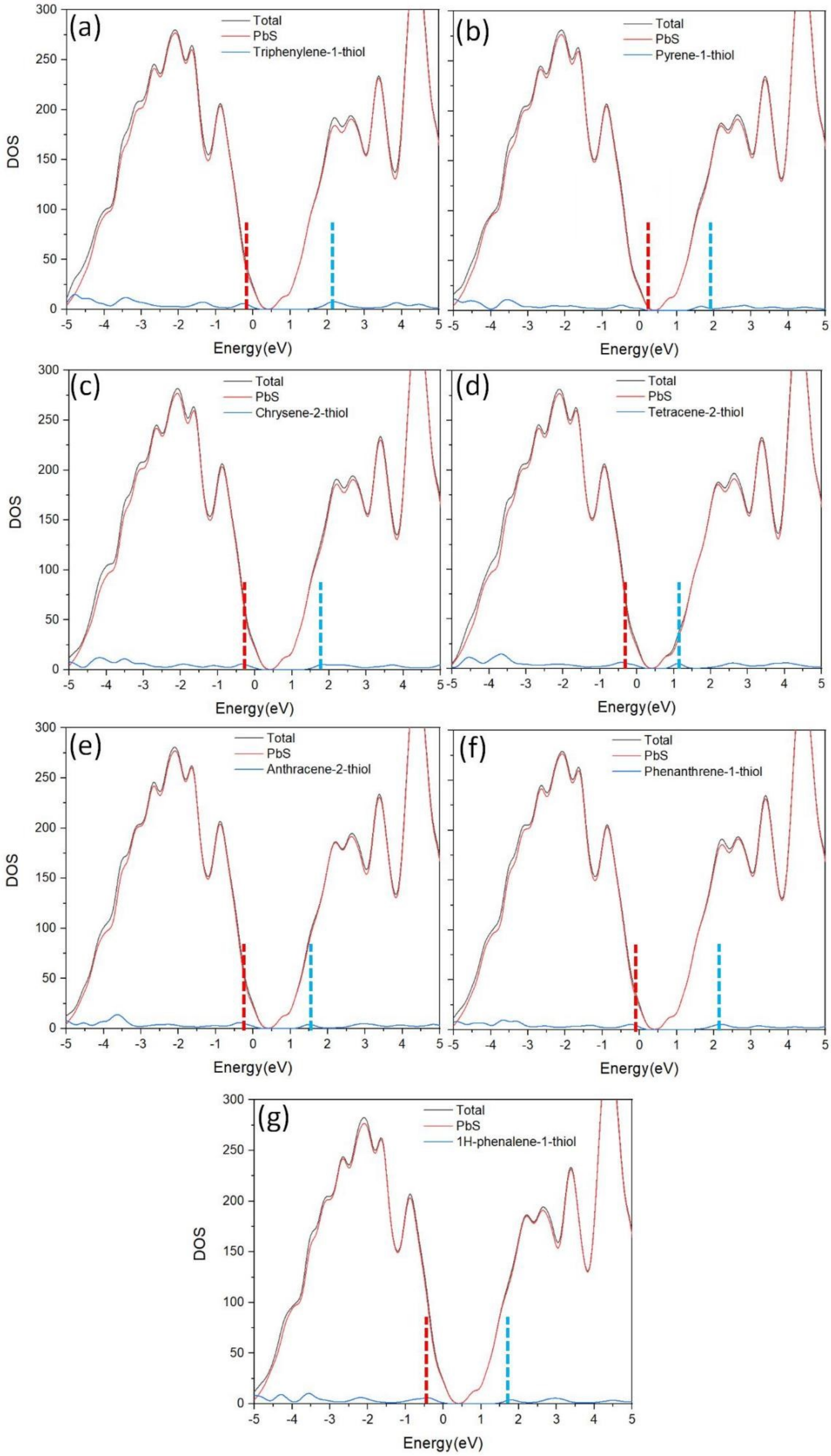

Figure S4. Total DOS and PDOS of the PbS (100) facet adsorbed with different PAHs molecules.The red dashed lines and blue dashed lines indicate the HOMO and LUMO of the molecules, respectively.

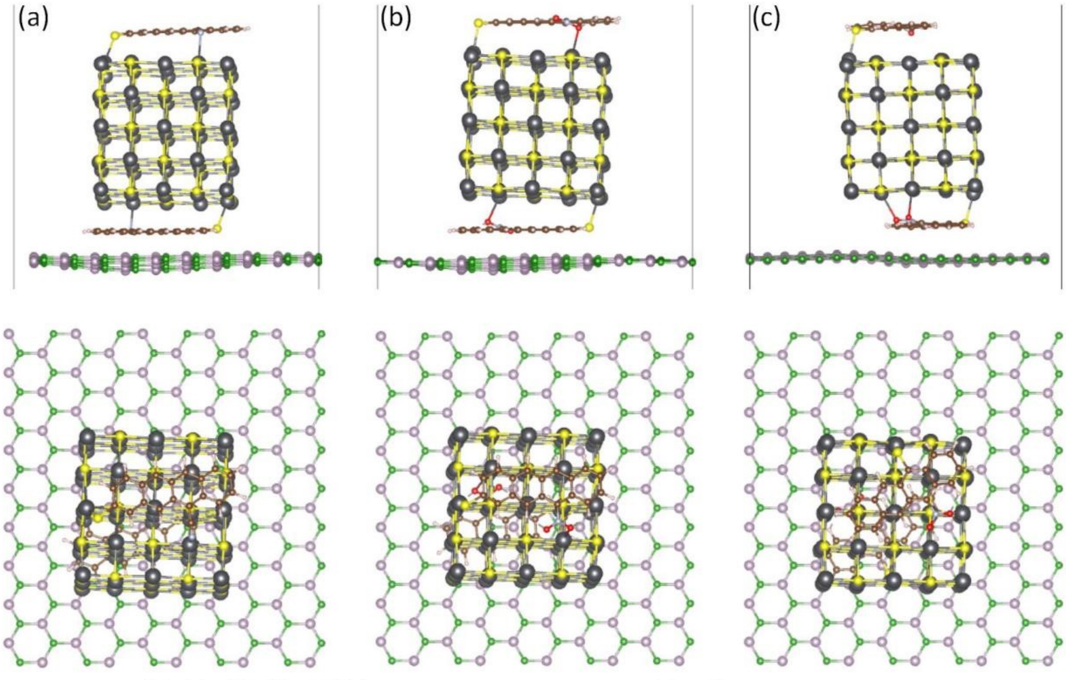

Figure S5. Structure-relaxed PbS QD-PAHs/BP systems: (a) Tetracene(cyano)-2-thiol; (b) Tetracene(nitro)-2-thiol; (c) Tetracene(nitro)-5-thiol.

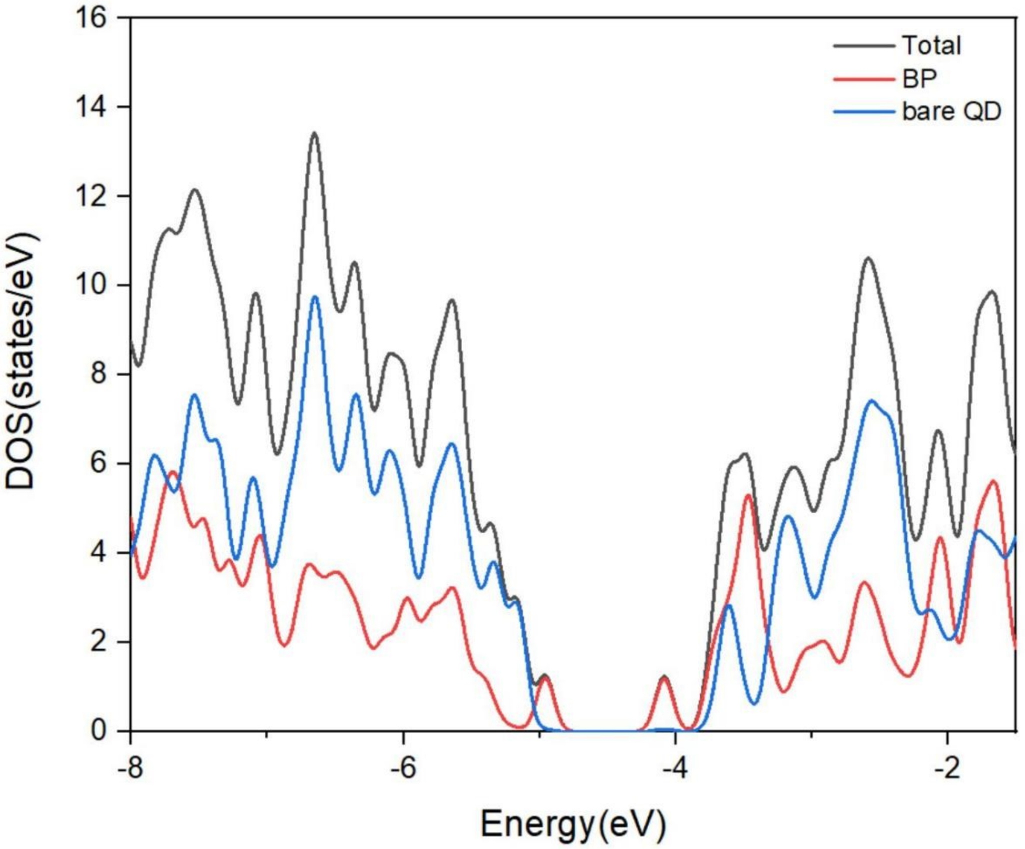

Figure S6. Total DOS and PDOS of the bare QD/BP system.

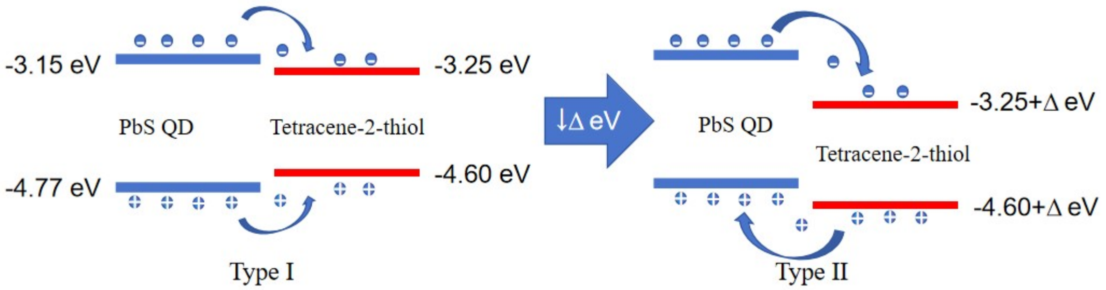

Figure S7. After the energy levels of the Tetracene-2-thiol molecule shift to deeper levels by Δ(≤ -0.17 eV), the energy level alignment between PbS QDs and Tetracene-2-thiol will change from Type I to Type II. Electrons from PbS QDs can transfer to Tetracene-2-thiol, while holes will be confined in the PbS QDs.

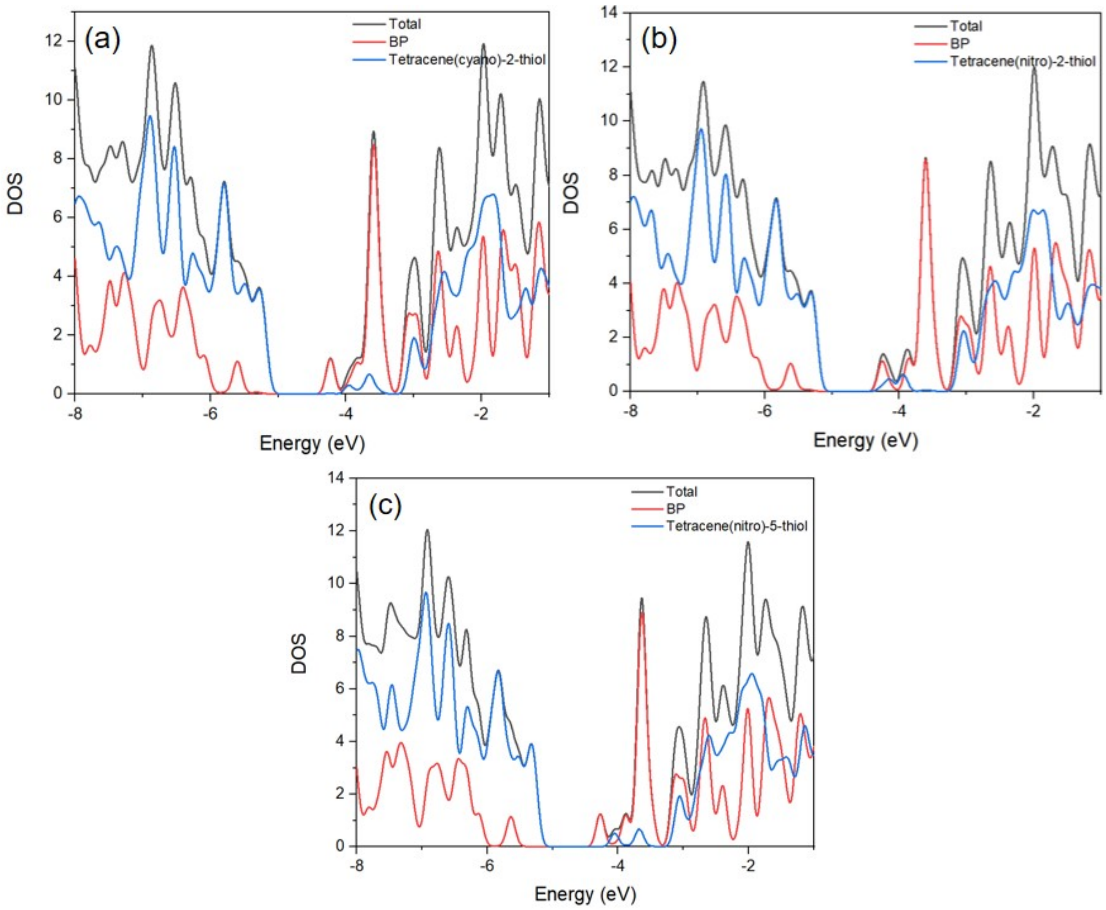

Figure S8. Total and projected DOS for the PbS QD systems with adsorbed Tetracene molecules, corrected using the HSE06 hybrid functional: (a) Tetracene(cyano)-2-thiol, (b) Tetracene(nitro)-2-thiol, (c) Tetracene(nitro)-5-thiol.

Table S1. Frontier orbital energies (E in eV) for three HSE06 hybrid functional-corrected PbS QD/BP hybrid systems:

	Tetracene(cyano)-2-thiol	**Tetracene(nitro)-2-thiol**	**Tetracene(nitro)-5-thiol**
E(BP VBM)	-5.61	-5.62	-5.64
E(BP CBM)	-4.23	-4.26	-4.28
E(PbS QD-PAHs HOMO)	-5.28	-5.31	-5.33
E(PbS QD-PAHs LUMO)	-3.97	-4.15	-4.06

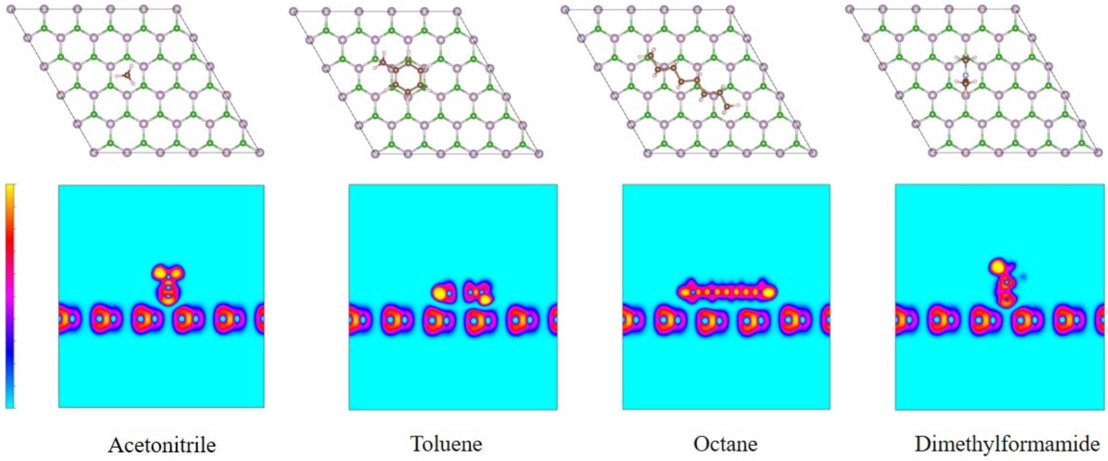

Figure S9. Structures of four solvent molecules adsorbed on the 2D BP surface (top) and the corresponding ELF (Electron Localization Function) plots (bottom). The yellow region represents strong electron localization, and the light blue region represents no electron localization.

Table S2. Adsorption and binding energies of four solvent molecules on the 2D BP surface

	Acetonitrile	Toluene	Octane	Dimethylformamide
Adsorption energy	-0.15	-0.46	-0.65	-0.23
Binding energy	-0.15	-0.47	-0.66	-0.23

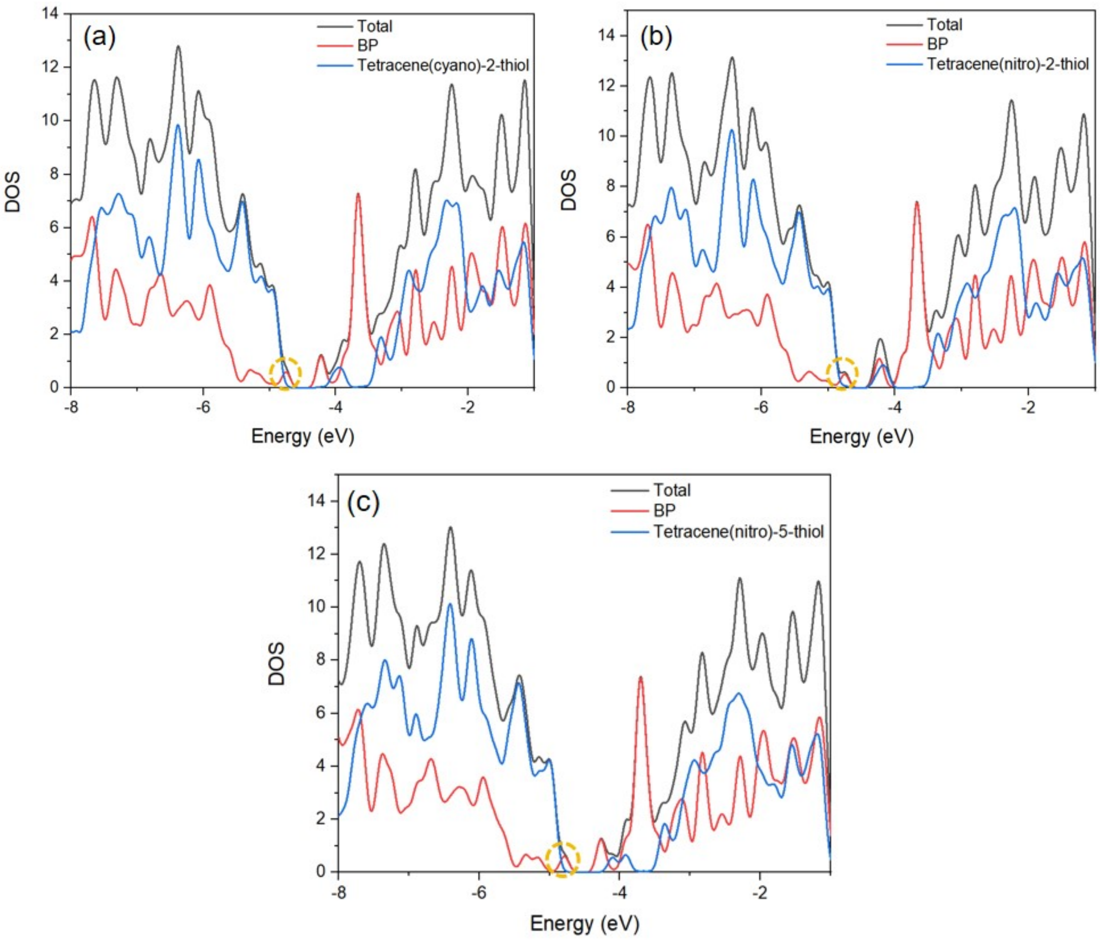

Figure S10. Total and projected DOS for the PbS QD systems with adsorbed Tetracene molecules, after introducing BP defects: (a) Tetracene(cyano)-2-thiol, (b) Tetracene(nitro)-2-thiol, (c) Tetracene(nitro)-5-thiol(The defect state density is marked by a yellow dashed line circle.).

[1]Du N, Cui Y, Zhang L, et al. Effect of Mn doping on the electron injection in CdSe/TiO 2 quantum dot sensitized solar cells[J]. Physical Chemistry Chemical Physics, 2021, 23(1): 647-656.
[2]Du N, Cui Y, Zhang L, et al. First-Principles Study of the Electron–Hole Recombination Rate at the Interface of the CdSe Quantum Dot and TiO2 Substrate[J]. The Journal of Physical Chemistry C, 2021, 125(29): 15785-15795.
[3]Zhou Q, Li B, Su X, et al. Tuning the electron transfer rates in near-infrared PbS quantum dots-anthraquinones complex by different chlorine-substituted[J]. Journal of Luminescence, 2022, 244: 118705.