SUPPORTING INFORMATION

Mitigating triplet loss in 2D WSe_2/non-fullerene heterostructures using halogenated acceptors

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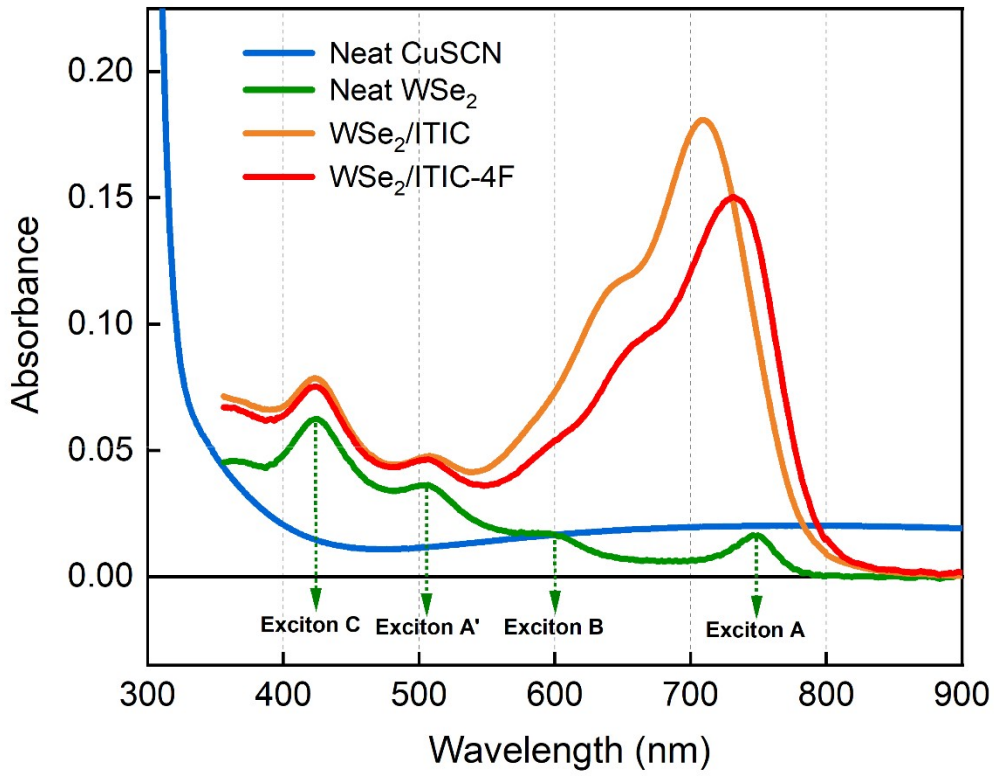

Figure S1. **Steady state absorption spectra**. Steady state optical absorption spectra of donor materials, monolayer WSe_2, CuSCN (~100 nm) and ML-WSe_2/NFA bilayers.

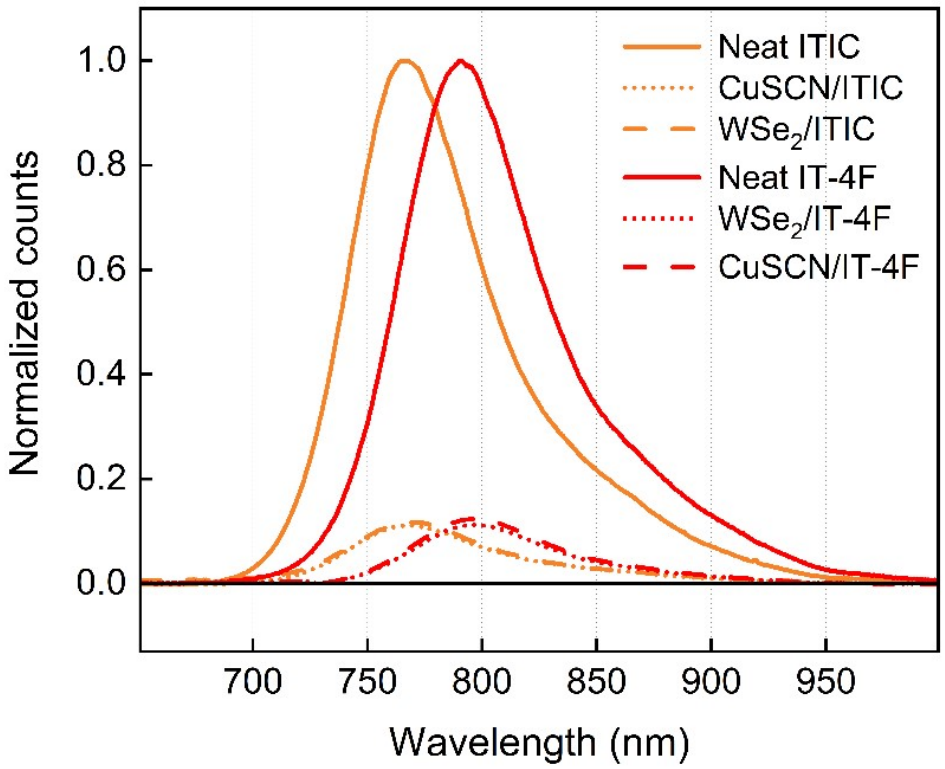

Figure S2. **Photoluminescence quenching in bilayers**. Steady state photoluminescence quenching measurements in various bilayers (CuSCN/ITIC, WSe_2/ITIC, CuSCN/IT-4F, and WSe_2/IT-4F).

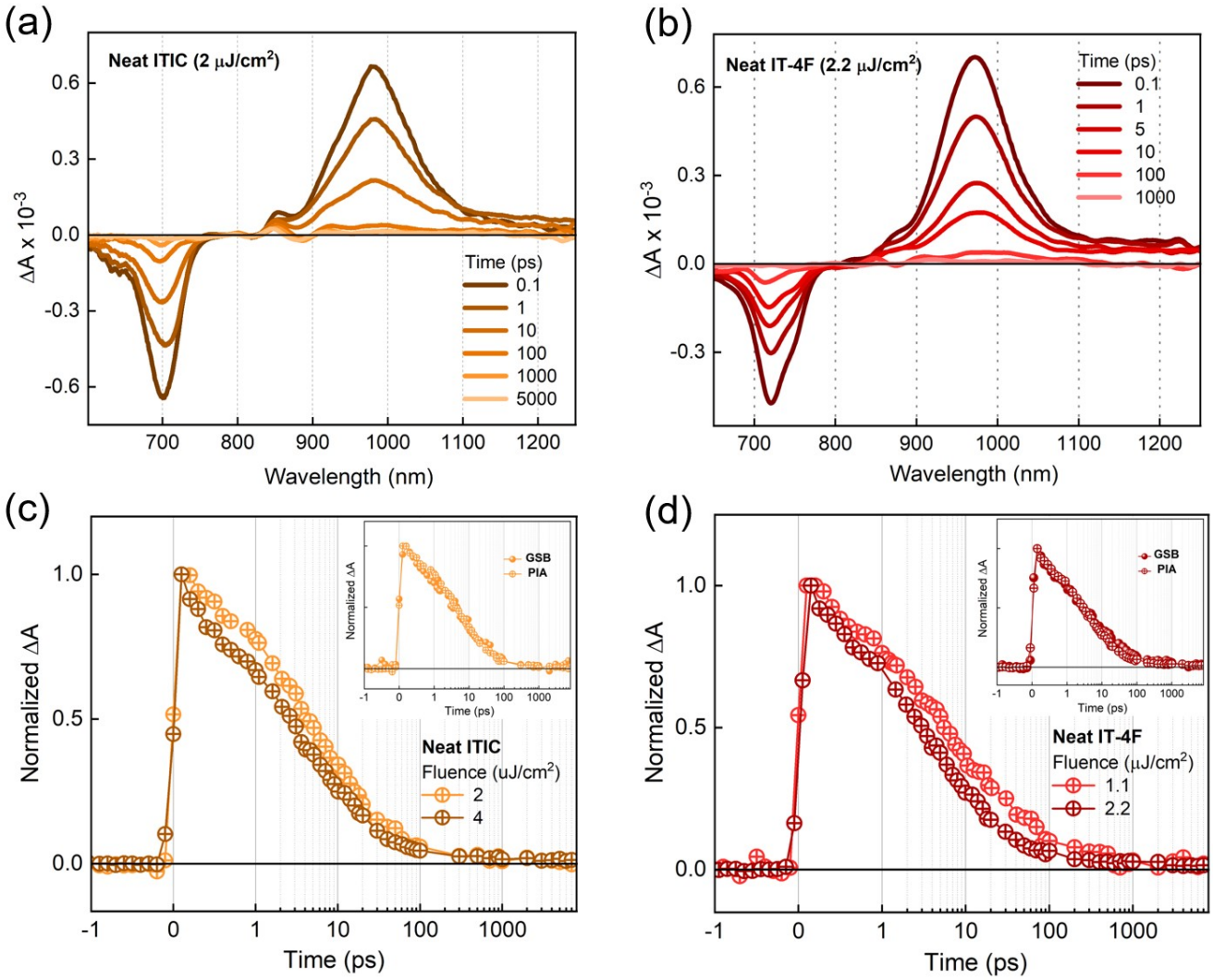

Figure S3. **Transient absorption in neat NFA films.** Series of transient absorption spectra of neat NFAs, (a) ITIC and (b) IT-4F, all excited at a pump wavelength of 700 nm and at fluence of ~2 μJ/cm^2, and fluence dependent exciton dynamics of neat NFAs (c) ITIC and (d) IT-4F. The inset figures show the corresponding dynamics of ground state bleach (GSB) and photoinduced absorption (PIA) features.

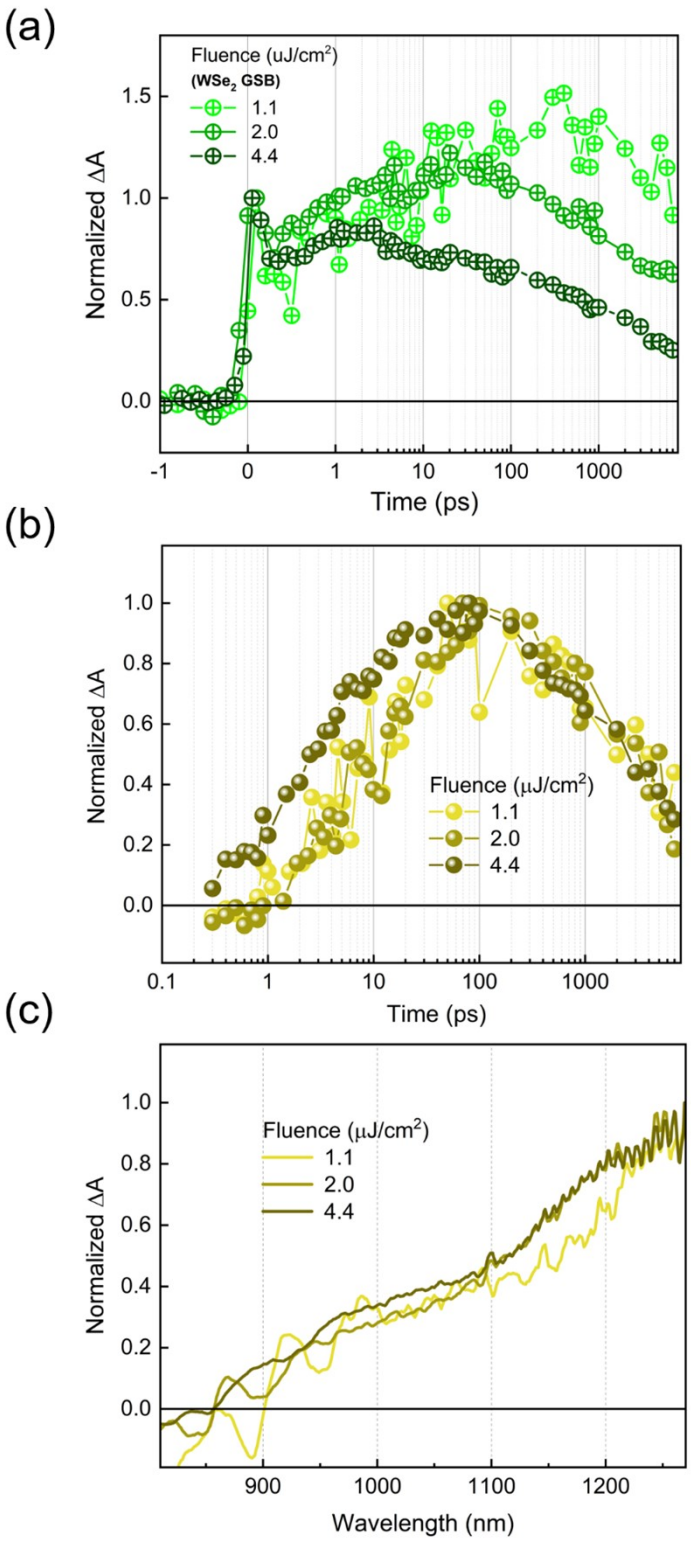

Figure S4. **Formation of triplet excitons from charges**. (a) Fluence dependent kinetics of holes, probed at WSe_2 hole GSB at 745 nm, (b) fluence dependent kinetics and (c) spectra of triplet excitons obtained after spectral decomposition in the 800-1270 nm region using MCR-ALS algorithm.

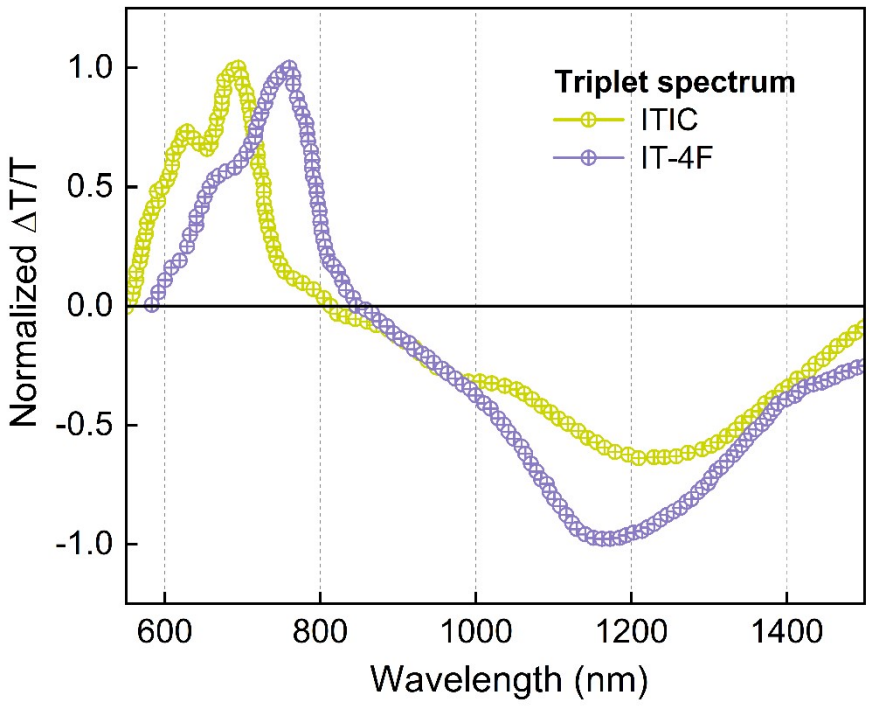

Figure S5. **Triplet sensitization in NFAs**. Normalized triplet spectra of NFAs, measured using steady state photoinduced absorption (PIA) (ITIC) and long delay TAS (IT-4F). The PIA measurements were carried out on heavy metal (PtOEP) doped NFA film after an excitation at 510 nm and at a temperature of 80 K, while long delay TAS measurements were done by exciting the films at 532 nm under vacuum.

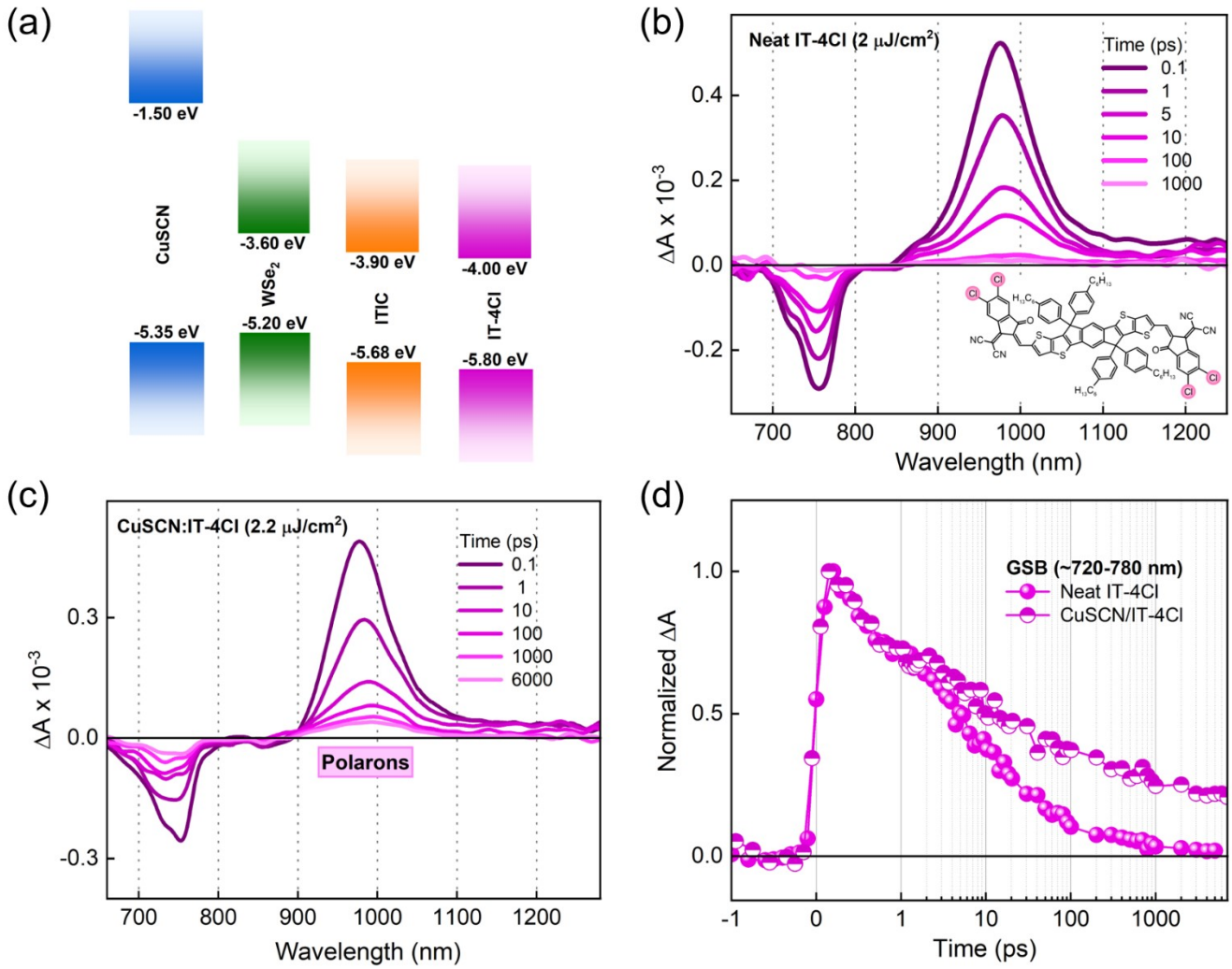

Figure S6. **Charge generation in bilayer with IT-4Cl**. (a) Energy level diagram of donor materials, CuSCN, ML-WSe_2, and acceptors ITIC and IT-4Cl, series of transient absorption spectra of (b) neat IT-4Cl (molecular structure is shown in the inset) and (c) CuSCN/IT-4Cl, and transient kinetics probed at the GSBs of neat IT-4Cl and CuSCN/IT-4Cl (all excited at 700 nm and at a pump fluence of 2.2 μJ/cm^2.)

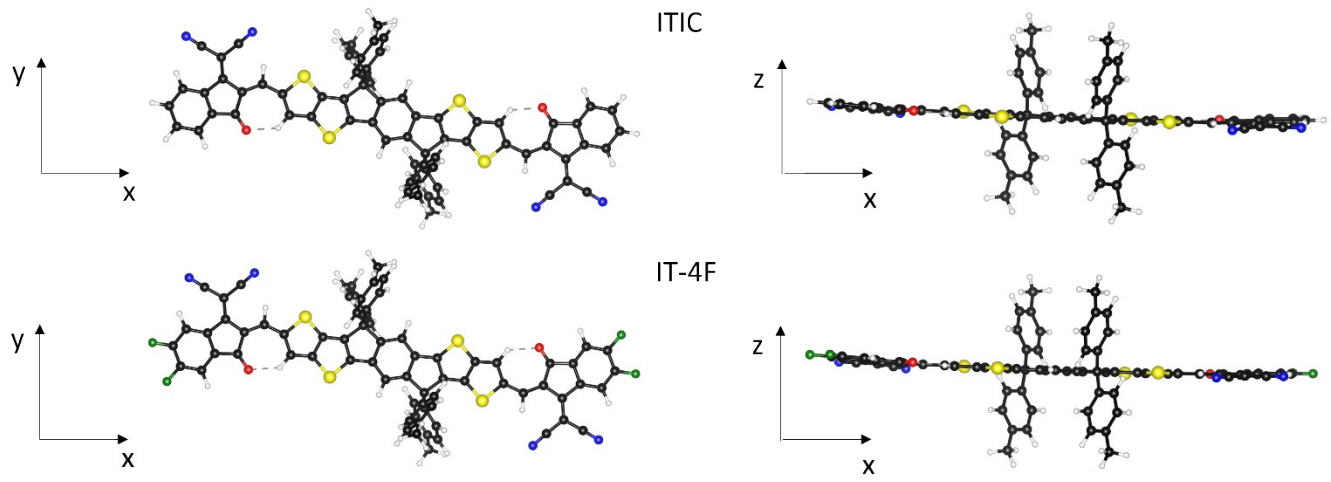

Figure S7: Ball-and-stick representation of isolated ITIC molecule (top) and its halogenated counterpart, IT-4F (bottom) relaxed *in vacuo*. C atoms are depicted in dark grey, H atoms in white, F atoms in green, O atoms in ref, N atoms in blue, and S atoms in yellow.

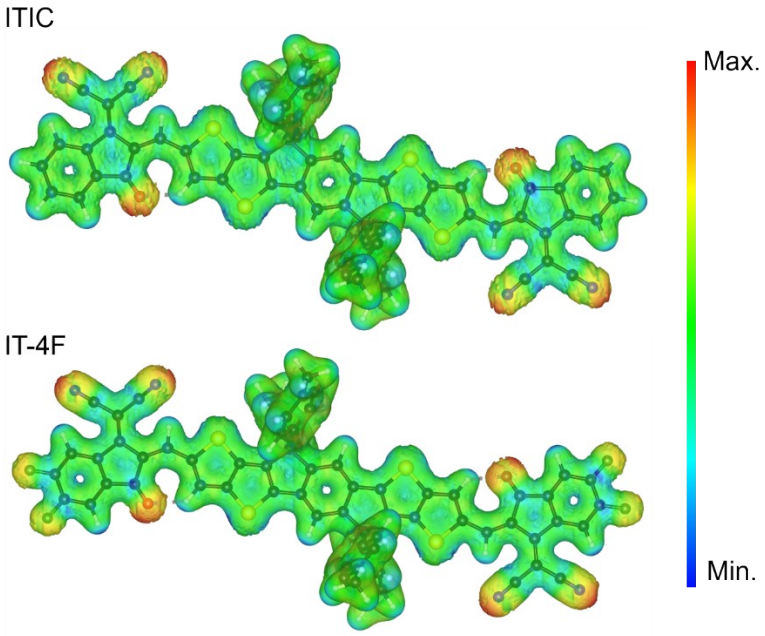

Figure S8: Electrostatic potential calculated for ITIC (top) and IT-4F (bottom) in the gas phase.

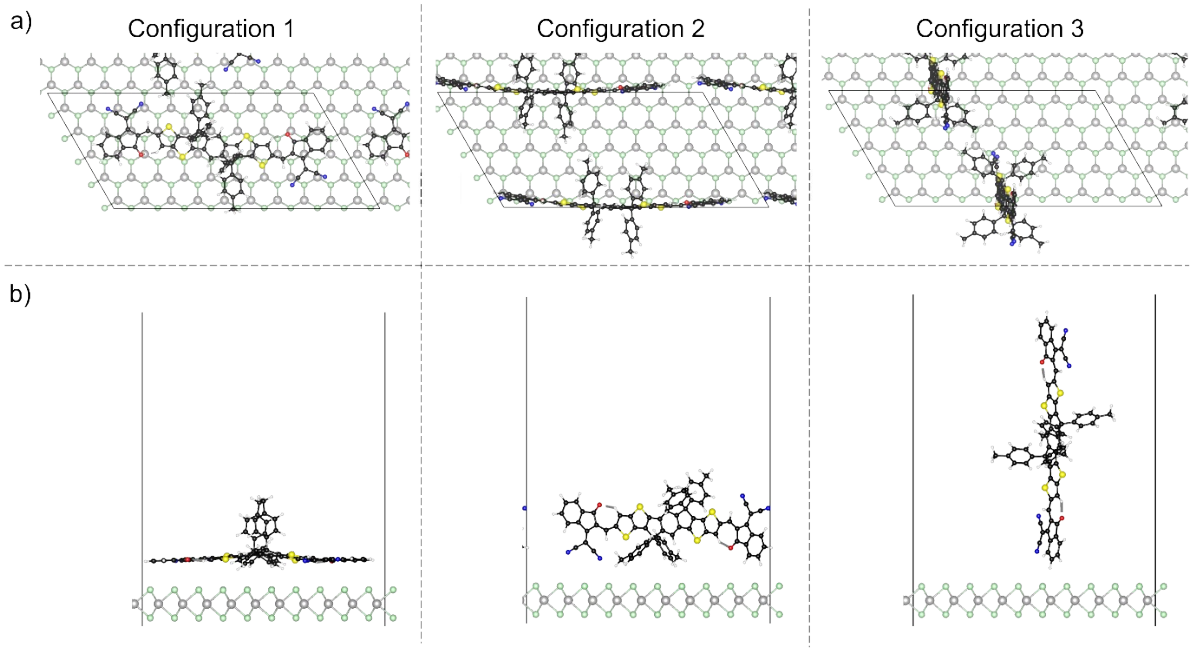

Figure S9: a) Top and b) side view of the optimized structures of the hybrid interface formed by ITIC adsorbed on monolayer WSe_2 in three different configurations. The grey continuous lines mark the lateral supercell boundaries. Configuration 1 is the most stable one with a total energy E_{tot} = -29420700, 930 eV followed by Configuration 2 (E_{tot} = -29420699, 854 eV) and Configuration 3 (E_{tot} = -29420699, 160 eV). Based on these results, we focus solely on Configuration 1 in the analysis of the electronic structure.

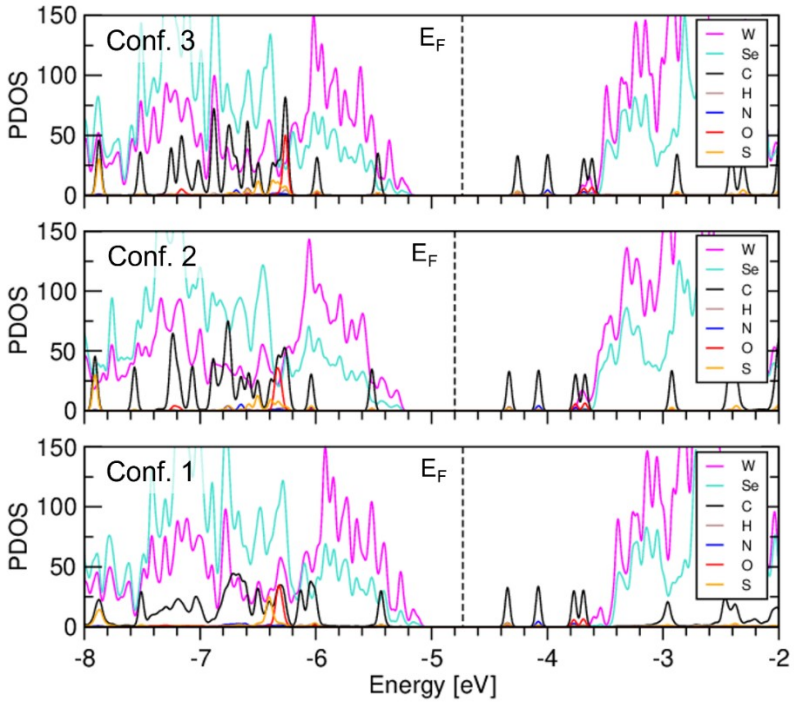

Figure S10: Projected density of states (PDOS) of ITIC adsorbed on ML-WSe_2 (10x5) supercell in three different configurations (Fig.S9) calculated with PBE functional. A Gaussian broadening of 20 meV is applied in all plots.

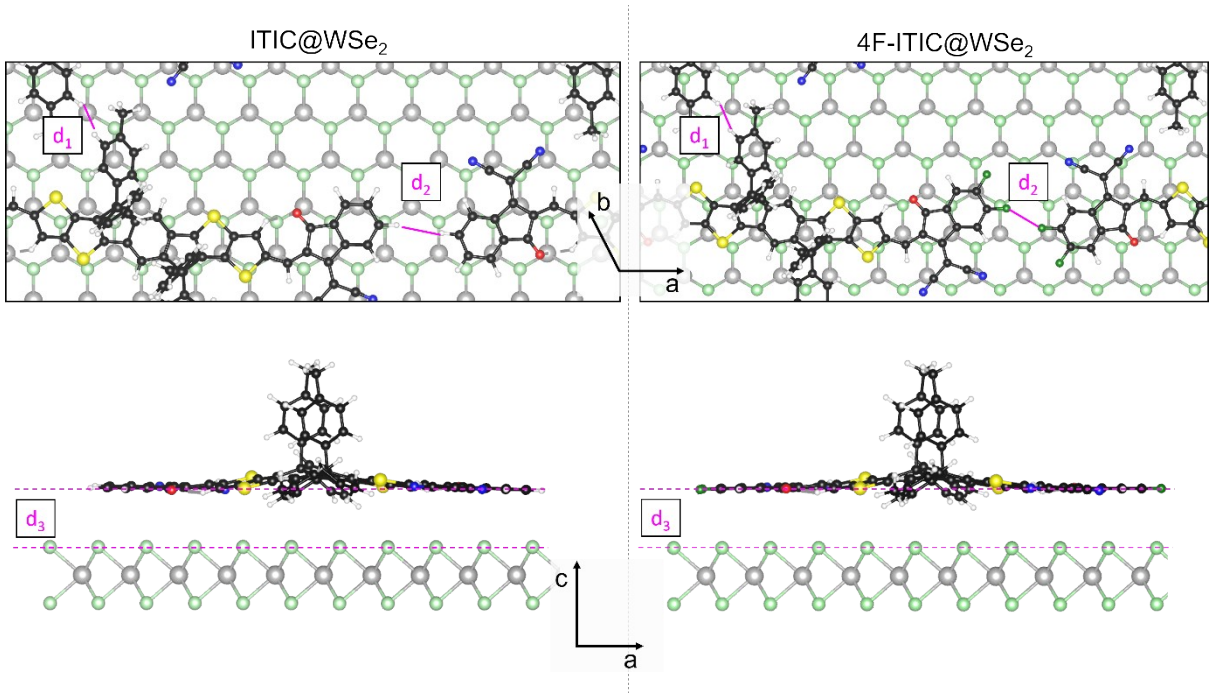

Figure S11: Optimized structures of WSe_2/ITIC (left panel) and WSe_2/IT-4F (right panel). d_1 is the shortest lateral distance between the H atoms in the aromatic carbon rings (**b**-direction), d_2 is the same distance in the **a**-direction, and d_3 the average distance between the molecule and the Se atoms in WSe_2.

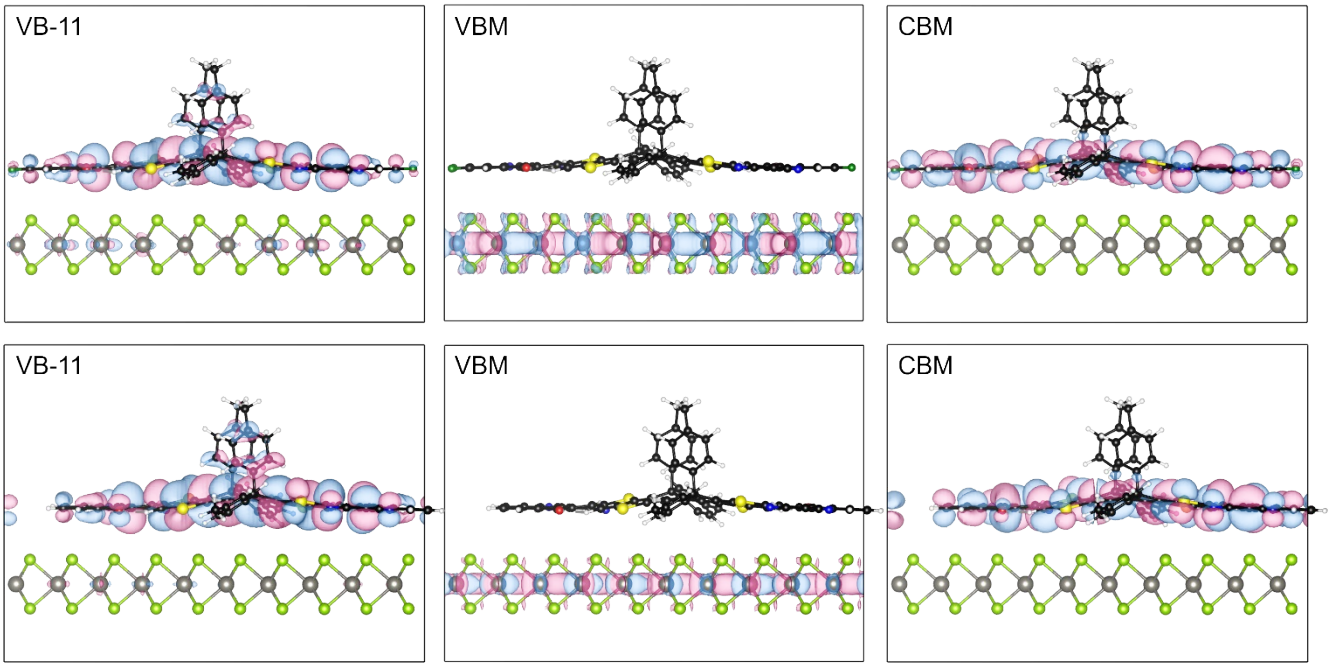

Figure S12: Selected electronic states of WSe_2/IT-4F (upper panels) and WSe_2/ITIC (lower panels) visualized by their isosurfaces (10% of the maximum value) at the Γ-point. CBM stands for the conduction band minimum and VBM for the valence band maximum.

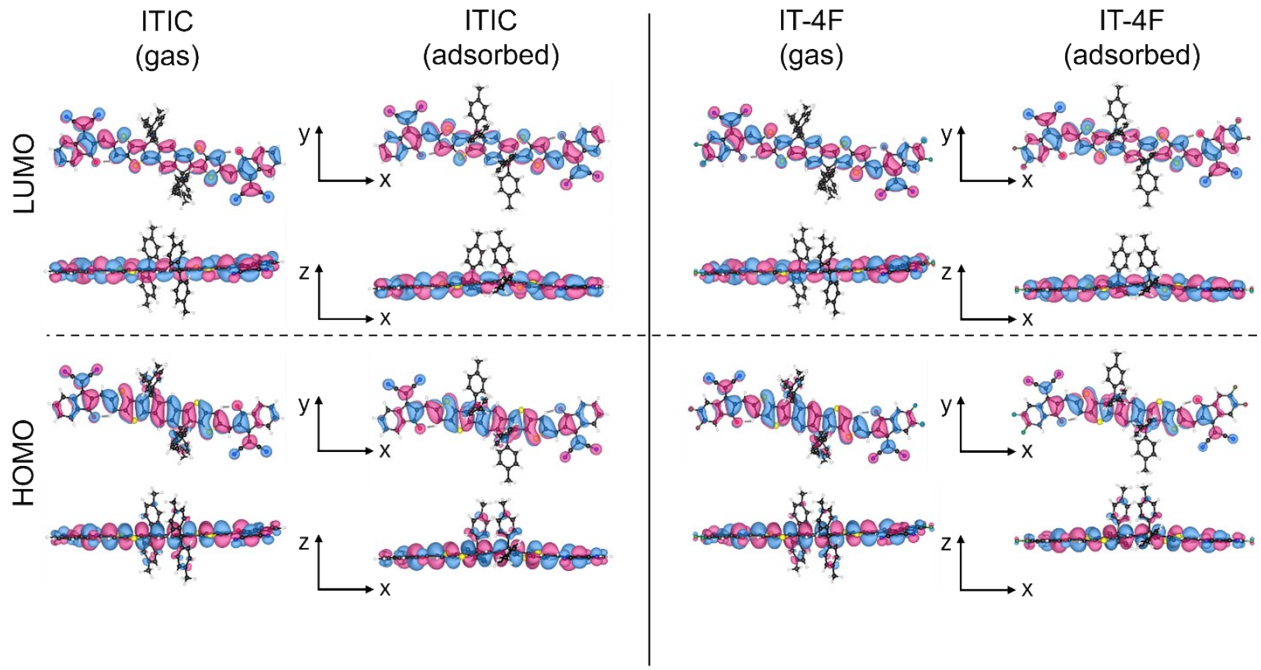

Figure S13: Side and top view of the HOMO (highest occupied molecular orbital) and the LUMO (lowest occupied molecular orbital). ITIC (left panels) and IT-4F (right panels) visualized by their isosurfaces (10% of the maximum value). In the gas-phase molecules in their optimized geometries and constrained in the geometry they assumed upon adsorption on WSe_2 (adsorbed).

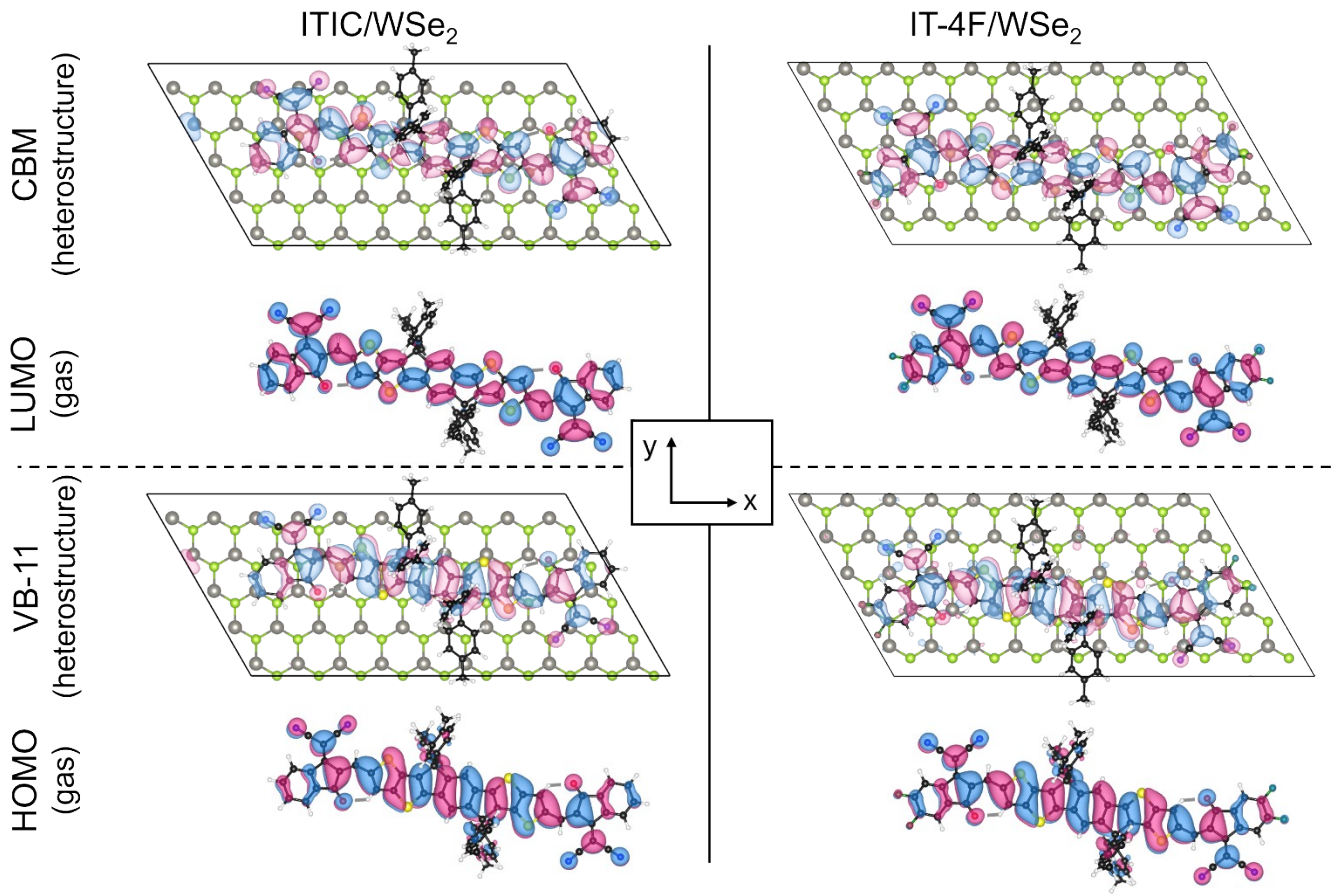

Figure S14: Top view of the HOMO (VB-11) and the LUMO (CBM) of NFA in gas-phase (herostructure). Left panel ITIC and ITIC/WSe_2 and right panel IT-4F and ITIC/WSe_2 visualized by their isosurfaces (10% of the maximum value).

Non-fullerene acceptor (NFA)	Absorption coefficients (10^5 cm^{-1})	Monomolecular lifetime (ps)	Exciton diffusion length (nm)
ITIC	1.10	394	31.9
IT-4F	1.16	351	47.4

Table S1. Summary of selection parameters of NFAs. Absorption coefficients, monomolecular exciton lifetimes and exciton diffusion lengths of NFAs, ITIC and IT-4F[1][2][3].

	d_1	d_2	d_3
WSe_2/ITIC	2.08	2.84	3.5
WSe_2/4F-IT	2.05	2.76	3.5

Table S2: Lateral (d_1 and d_2) and vertical distance (d_3) between the molecule and the monolayer in the considered hybrid heterostructures see **Figure S10**. All values are given in Å.

	ITIC@WSe_2	ITIC (absorbed)	ITIC (gas-phase)	IT-4F@WSe_2	IT-4F (absorbed)	IT-4F (gas-phase)
HOMO [eV]	-5.30	-5.59	-5.61	-5.34	-5.74	-5.76
LUMO [eV]	-4.25	-4.00	-3.94	-4.34	-4.17	-4.12
E_{gap} [eV]	1.05	1.59	1.67	1.00	1.57	1.64
Dipole moment [Debye]		3.76	0.79		3.80	0.26

Table S3: Frontier energy values and energy gap (E_{gap}) computed from DFT (HSE06+SOC functional) for the hybrid interfaces and the gas-phase molecules in their optimized geometries and constrained in the geometry they assumed upon adsorption on WSe_2 (adsorbed).

NFAs	E_{S1}	E_{T1}	$\Delta E_{ST} = E_{S1} - E_{T1}$
ITIC	1.85 eV	1.22 eV	0.63 eV
IT-4F	1.82 eV	1.21 eV	0.61 eV

Table S4: Results obtained within the density functional theory (DFT) and time-dependent DFT (TDDFT) framework to study the optical properties of NFAs molecules. All TDDFT calculations are performed using the Gaussian 16 package[4]. We used the Becke three-parameter Lee–Yang–Parr (B3LYP)[5] and Gaussian-type cc-pVTZ basis set[6]. E_{S1} is the first singlet excitation, E_{T1} is the first triplet excitation, and ΔE_{ST} is the energy difference between T_1 and S_1 states.

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