SUPPORTING INFORMATION

Photoluminescence Quenching in WSe_2 via p-Doping Induced by Functionalized Rylene Dyes

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Synthesis of CN_4PMI

5,8,9,11-tetrabromo-1H,3H-benzo[10,5]anthra[2,1,9-def]isochromene-1,3-dione (100 mg, 0.157 mmol, 1.0 equiv) was dissolved in anhydrous N-methyl-2-pyrrolidone (NMP, 5 mL) and the solution was degassed by argon sparging for 15 min. Zinc acetate [$Zn(OAc)_2$] (288 mg, 1.57 mmol, 10 equiv) and copper(I) cyanide (CuCN; 225 mg, 2.51 mmol, 16 equiv) were added, and the mixture was heated to 130°C. After 10 min under argon, a second portion of CuCN (225 mg, 2.51 mmol, 16 equiv; 32 equiv total) was added and the suspension was stirred at 130°C for 15 min. n-Octylamine (0.26 mL, 1.57 mmol, 10 equiv) was added dropwise and the reaction was maintained at 130°C for 15 min, then cooled to room temperature. Water (10 mL) was added; the precipitate was collected by filtration, washed thoroughly with water, and dried under reduced pressure. The crude material was purified by flash chromatography on silica gel (SiO_2; eluent CH_2Cl_2) to obtain CN_4PMI as a dark solid (40 mg, 0.075 mmol, 48%).

CN_4PMI Characterization

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 9.49 (d, $J = 8.1$ Hz, 2H), 9.03 (s, 2H), 8.44 (d, $J = 8.1$ Hz, 2H), 4.21 (t, $J = 7.9$ Hz, 2H, NCH_2), 1.74 (p, 2H, CH_2), 1.46–1.25 (m, 10H), 0.90–0.87 (m, 3H, CH_3).

^{13}C NMR (75.5 MHz, $CDCl_3$, 298 K) δ 161.9, 161.4, 141.3, 139.5, 136.8, 135.9, 135.8, 133.4, 129.6, 128.7, 126.6, 111.9, 109.0, 41.2, 31.8, 29.3, 29.2, 28.0, 27.1, 22.6, 14.1.

HRMS (ESI) m/z calcd for $C_{34}H_{23}N_5O_2$: 533.1852 $[M]^+$; found: 533.1840.

Fluorescence (CH_2Cl_2, nm): $\lambda_{ex} = 475$.

Cyclic voltammetry

Cyclic voltammetry (CV) was performed on a potentiostat using a conventional three-electrode cell at 298 K. Solutions of CN_4PMI (0.50 mM) in CH_2Cl_2 containing 0.10 M

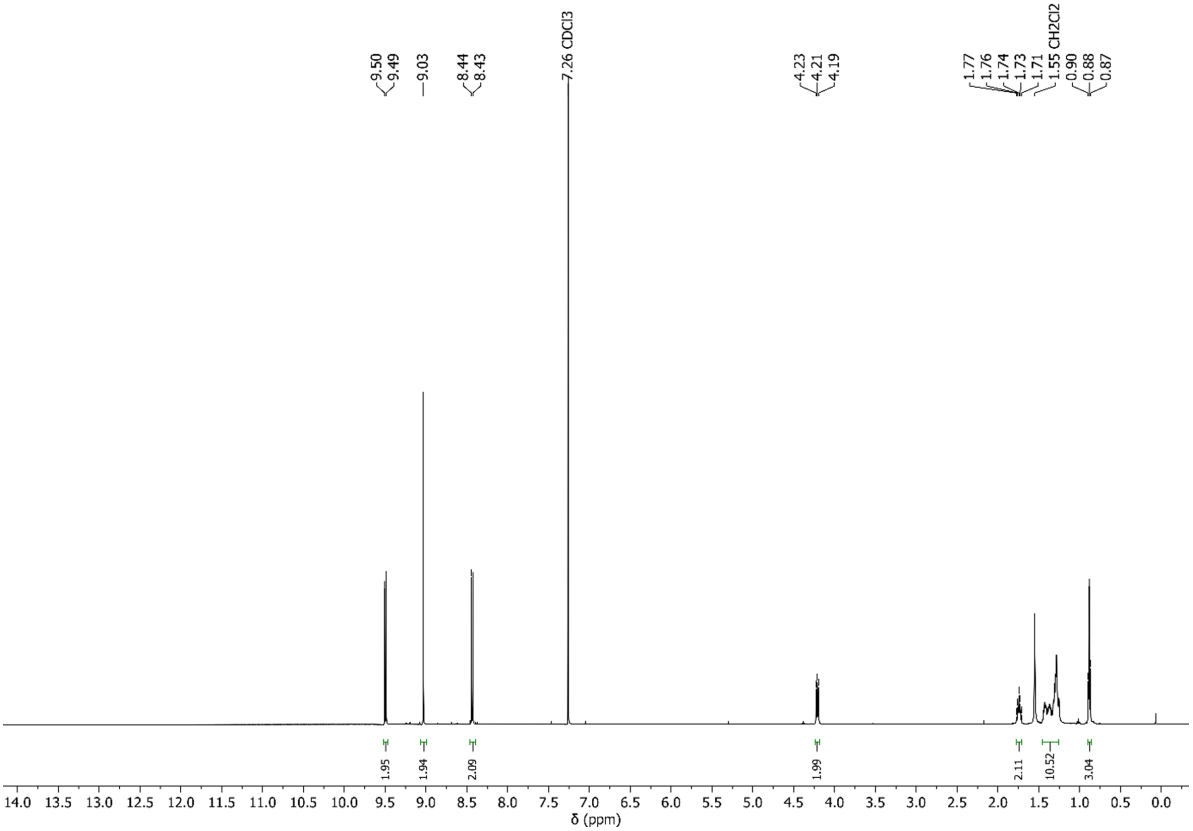

Figure S1: ^{1}H NMR spectrum of CN_4PMI ($CDCl_3$, 500 MHz, 298 K).

n-Bu_4NPF_6 were thoroughly deoxygenated by sparging with Ar for $\geq$ 15 min prior to each measurement and kept under Ar during scans. A glassy carbon disk served as the working electrode, Pt wire as counter, and Ag/AgCl as the reference electrode. Scan rates were 0.20, 0.40, 0.60, 0.80, 1.00, and 2.00 Vs$-$1. After each experiment ferrocene was added as an internal standard; all potentials are reported vs Fc/Fc^+. Data were baseline-corrected; peak potentials (E_p), half-wave potentials for reversible couples ($E^{\circ\prime} = (E_{p,a} + E_{p,c})/2$), and peak separations (ΔE_p) were obtained by standard procedures.

Table S1: Summary of Cyclic Voltammetry Data

Process	$\mathbf{E_{p,c}}$ **(V)**	$\mathbf{E_{p,a}}$ **(V)**	$\mathbf{\Delta E_p}$ **(mV)**	$\mathbf{E^{\circ\prime}}$ **(V)**	**Reversibility**
Red 1	-0.67	-0.57	~ 100	-0.62	quasi-reversible
Red 2	-1.04	-0.94	~ 100	-0.99	quasi-reversible
Ox 1	$+0.23$	—	—	—	irreversible

CN_4PMI shows two quasi-reversible reductions with $E^{\circ\prime} = -0.61$ V and -0.99 V and

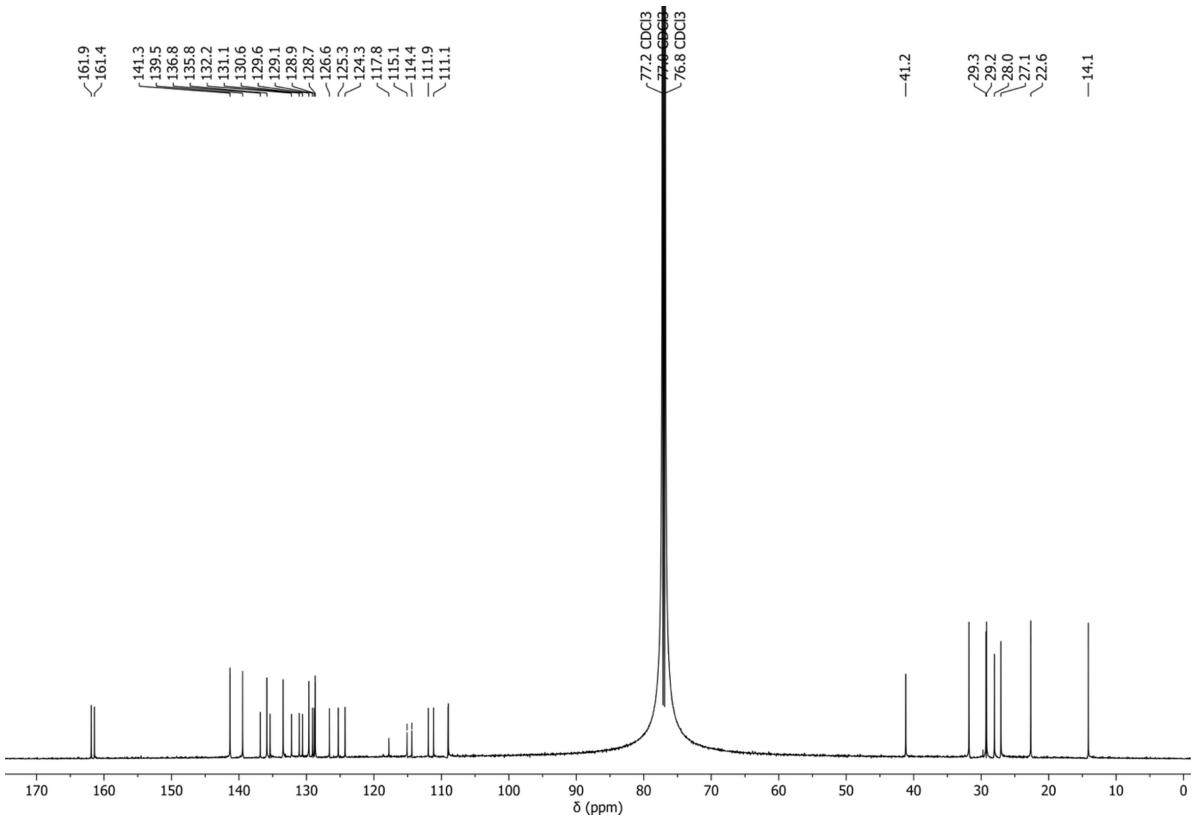

Figure S2: ^{13}C NMR spectrum of CN_4PMI ($CDCl_3$, 75 MHz, 298 K).

$\Delta E_p \approx 100$ mV for each couple (greater than the 57 mV expected for an ideal one-electron Nernstian process at 298 K), indicating electron transfer/quasi-reversibility at the chosen conditions. The corresponding cathodic peak potentials are $E_{p,c} = -0.67$ V (red1) and $E_{p,c} = -1.04$ V (red2). On the anodic side, an irreversible oxidation is observed at $E_p = +0.23$ V. Reduction of the medium begins near -2.0 V. The reduction steps are consistent with 1e$^-$. Using $Fc/Fc^+ = -4.80$ eV on the vacuum scale and onsets derived from CV: LUMO $= -5.47$ eV, HOMO $= -4.57$ eV.

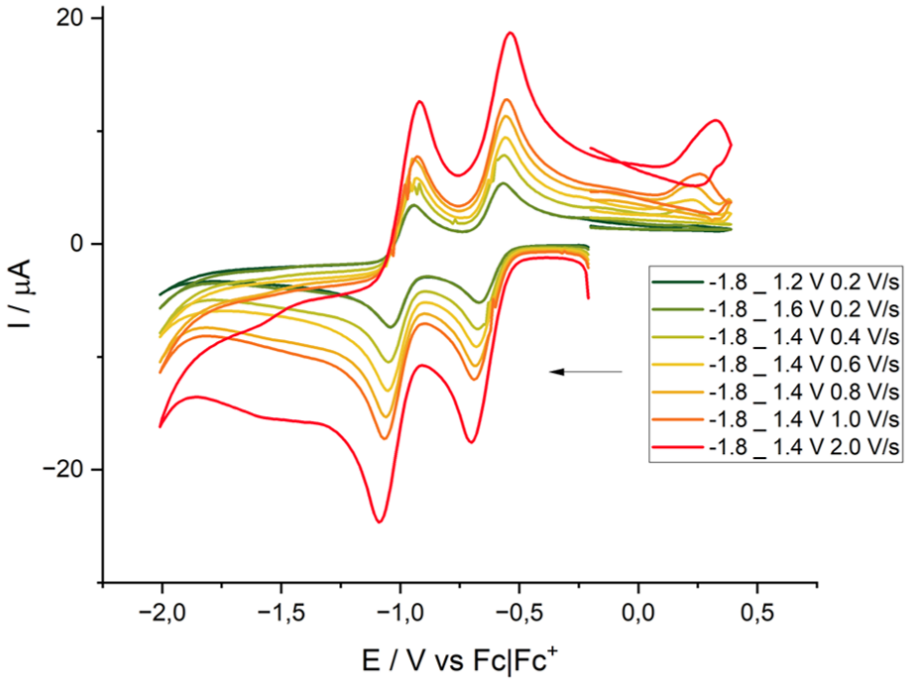

Figure S3: Cyclic voltammograms of CN_4PMI (0.50 mM) in CH_2Cl_2 (0.10 M n-Bu_4NPF_6) at 298 K using a 3 mm glassy-carbon working electrode, Pt wire counter electrode and Ag/AgCl pseudo-reference; potentials referenced to Fc/Fc^+ added at the end of each run. Scan rates: 0.2 - 2.0 Vs−1; initial scan toward negative potentials (arrow).

Additional Computational Results

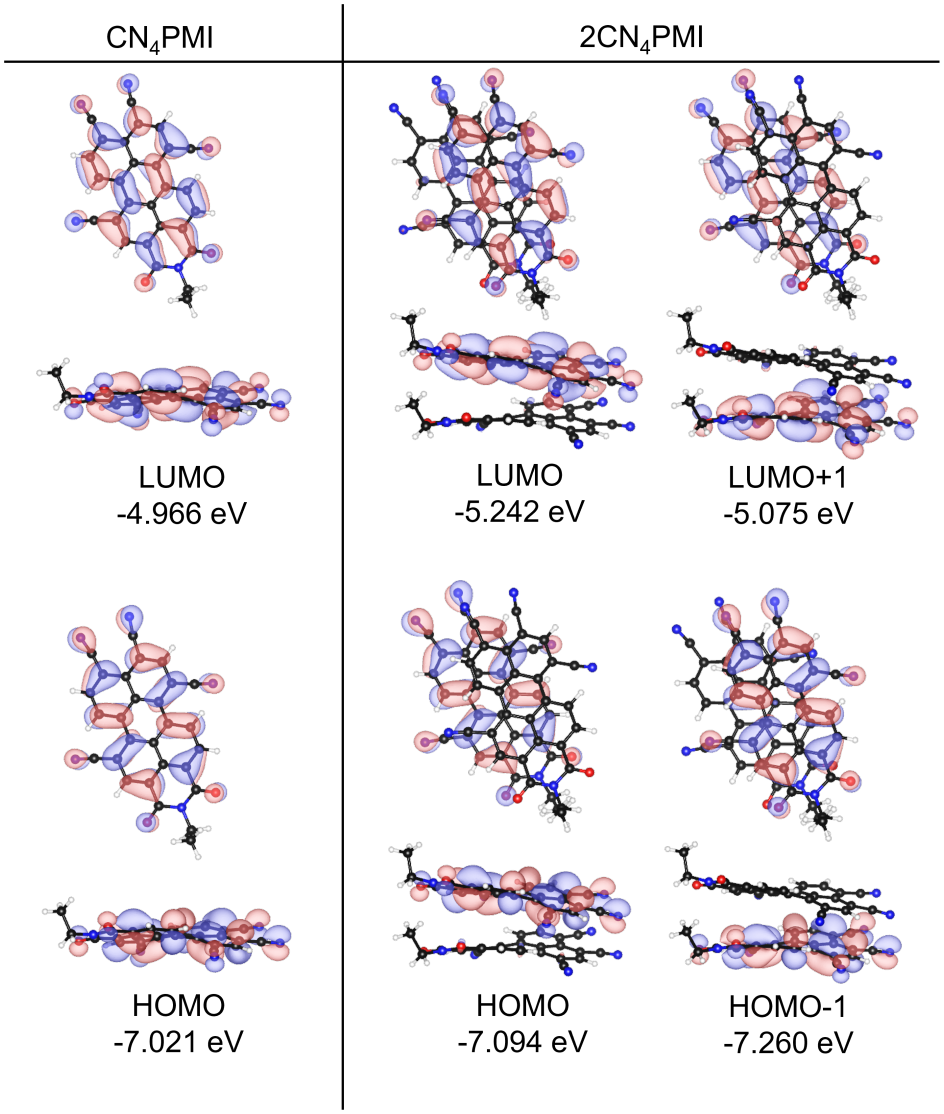

Figure S4: Molecular orbitals of CN_4PMI single molecule and bimolecular cluster ($2CN_4PMI$) in the gas phase. The iso-surfaces are 10% of the maximum value.

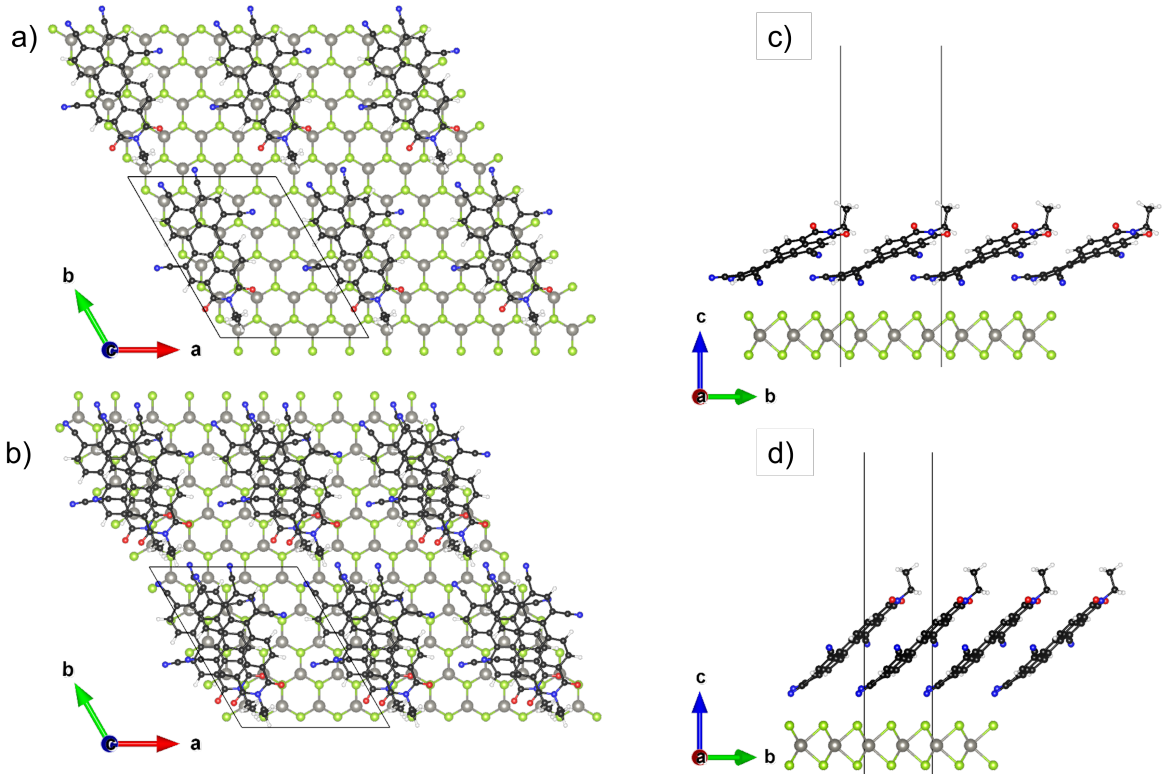

Figure S5: Periodic representation of the unit cell of $CN_4PMI@WSe_2$ hybrid interface. Flat-lying (a) and stacked (b) molecules adsorbed on WSe_2. Molecule forming an angle of 22° (c) and 43° (d) with respect to the WSe_2 plane.

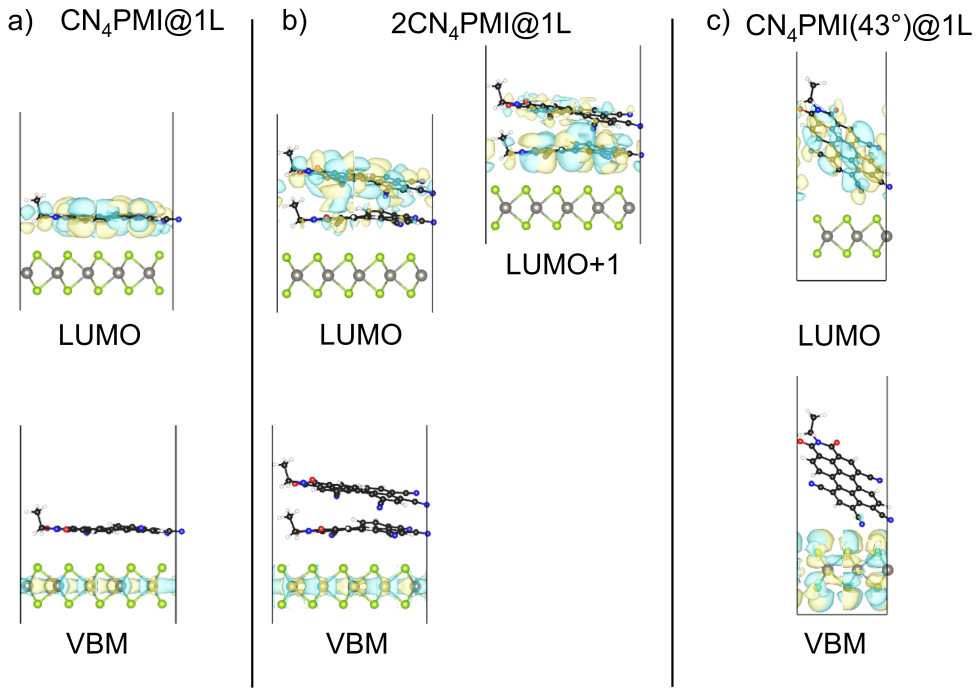

Figure S6: Side views of the real-space representation of valence band maximum (VBM) and lowest unoccupied molecular orbital (LUMO) of a) CN_4PMI:1L, b) 2(CN_4PMI):1L, and c) CN_4PMI(43°):1L systems (iso-surfaces equal to 10% of the maximum value)

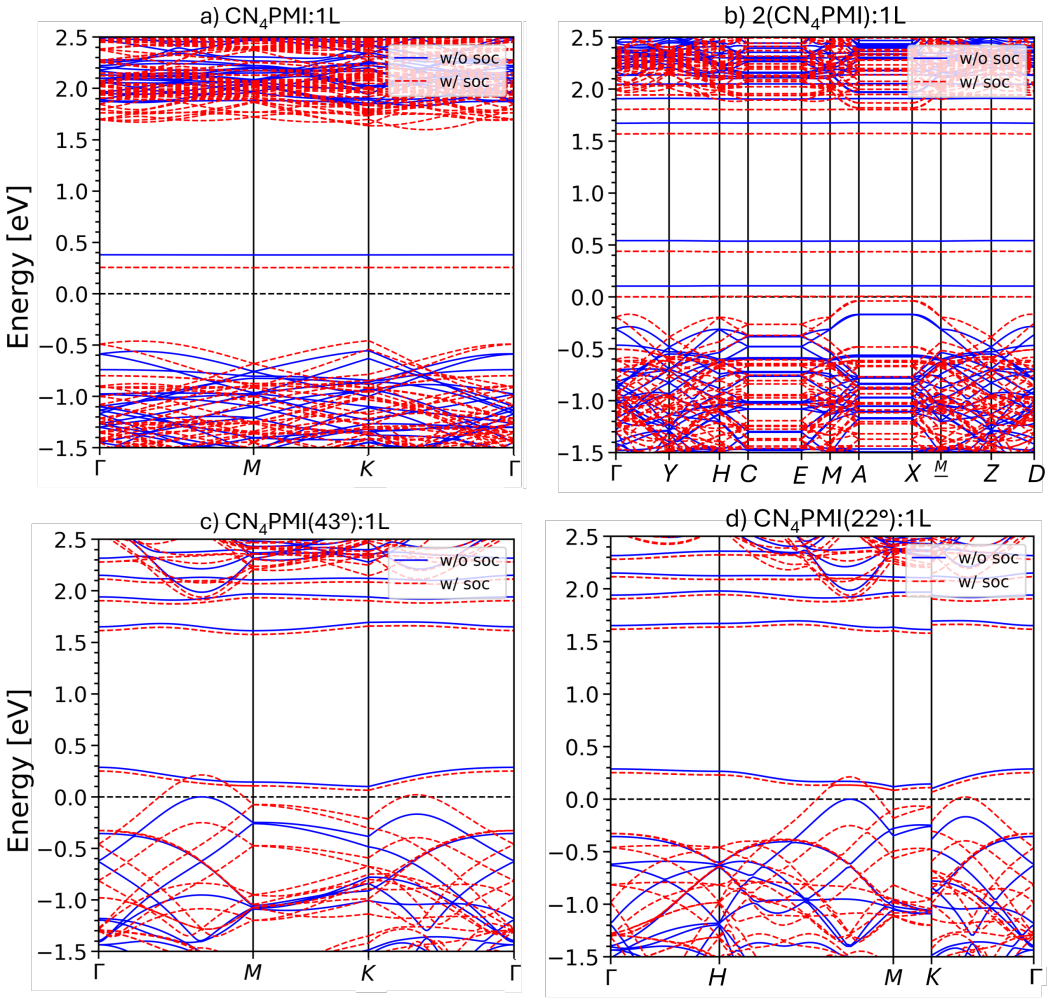

Figure S7: Band structures of a) CN_4PMI:1L, b) 2(CN_4PMI):1L, c) CN_4PMI(43°):1L, and d) CN_4PMI(22°):1L, computed from DFT (HSE06 functional) with and without spin-orbit coupling (SOC).

Optical Characterization of the WSe_2 Sample

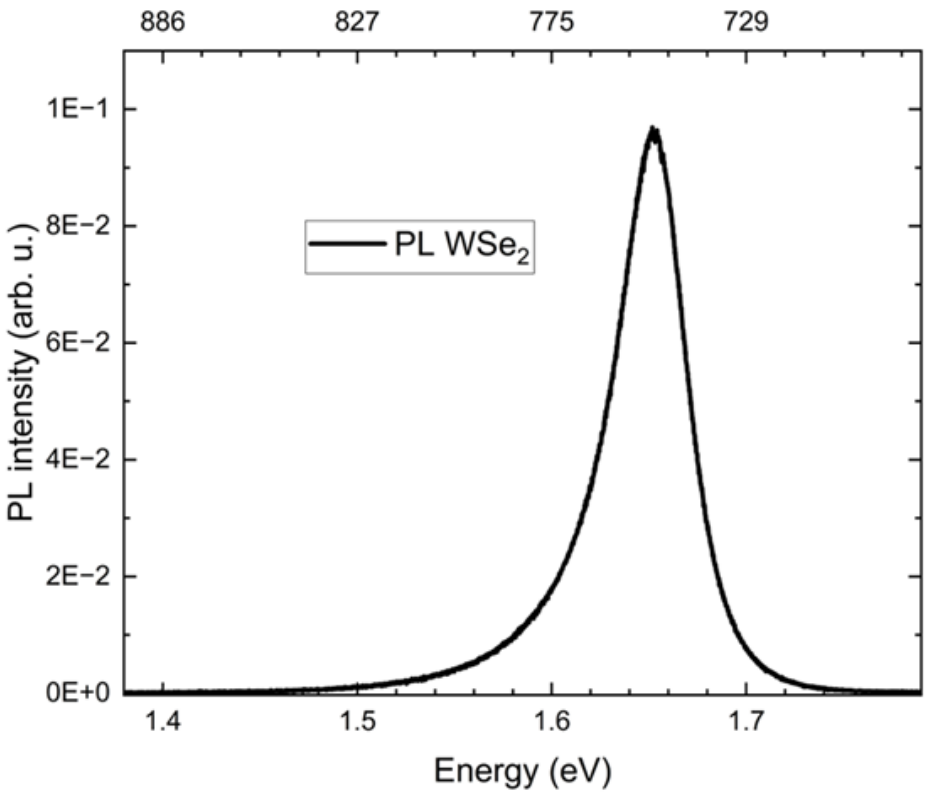

Figure S8: PL characterization of the WSe_2 sample. The sharp maximum at 1.67 eV without additional emission at lower energies confirms its monolayer nature.