

Supplementary Information File

Substrate-driven modulation of interfacial charge transfer dynamics in cobalt phthalocyanine–2D material van der Waals heterostructures.

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Captions

Fig. SI1. AFM topographic images of (a) CoPc–Gr, (b) CoPc–WS₂, and (c) CoPc–ReS₂ heterostructures acquired at different regions on each sample.

Fig. SI2. Raman spectra of CoPc–Gr (a), CoPc–WS₂ (b), and CoPc–ReS₂ (c) acquired at different positions on each sample.

Fig. SI3. XPS survey spectra of CoPc films deposited on (a) SiO₂, (b) WS₂, (c) graphene (Gr), and (d) ReS₂ substrates. In each spectrum, the photoemission peaks corresponding to the main constituent elements are clearly identified. All survey spectra were acquired using a photon energy of 930 eV.

Fig. SI4. (a) Fitting of the N K-edge NEXAFS spectra collected at 15° and 90° for the CoPc–Gr sample. (b) Corresponding fitting of the spectra acquired at the same incidence angles for the CoPc–WS₂ sample.

Fig. SI5. Resonant photoemission spectra (RPES) of CoPc deposited on SiO₂, graphene, WS₂, and ReS₂ substrates, recorded at excitation energies corresponding to the (a) N 1s → LUMO and (b) N 1s → LUMO+1 resonances. Each spectrum was obtained after subtraction of a pre-resonance spectrum to remove non-resonant background contributions.

Fig. SI6. Valence band spectra of (a) WS₂ and (b) ReS₂ used to determine the valence band maximum (VBM) position. The VBM edge was extracted by linear extrapolation of the leading edge of the valence band to the baseline, allowing the estimation of the energy offset between the two 2D materials.

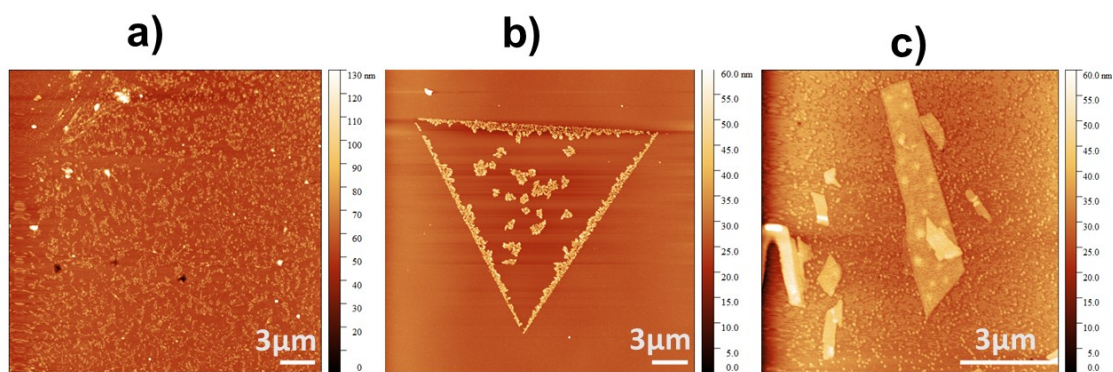


Fig. SI1. AFM topographic images of (a) CoPc–Gr, (b) CoPc–WS₂, and (c) CoPc–ReS₂ heterostructures acquired at different regions on each sample.

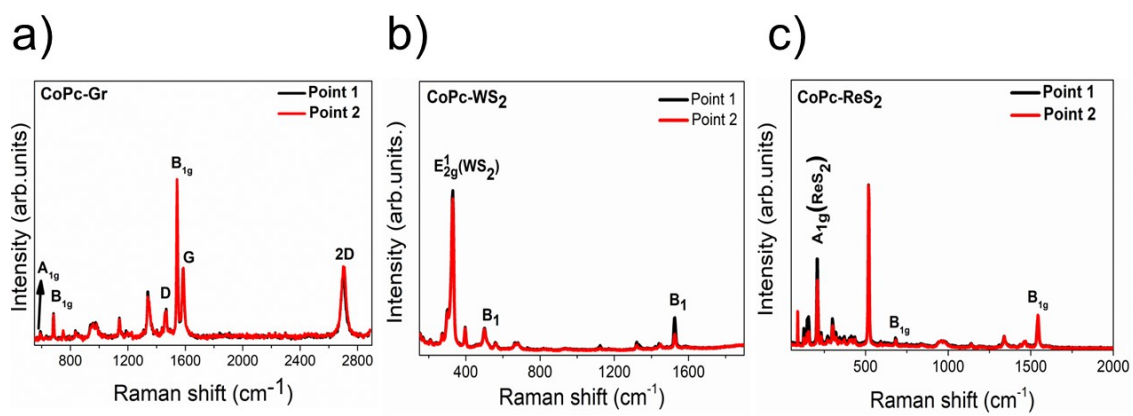


Fig. SI2. Raman spectra of CoPc–Gr (a), CoPc–WS₂ (b), and CoPc–ReS₂ (c) acquired at different positions on each sample.

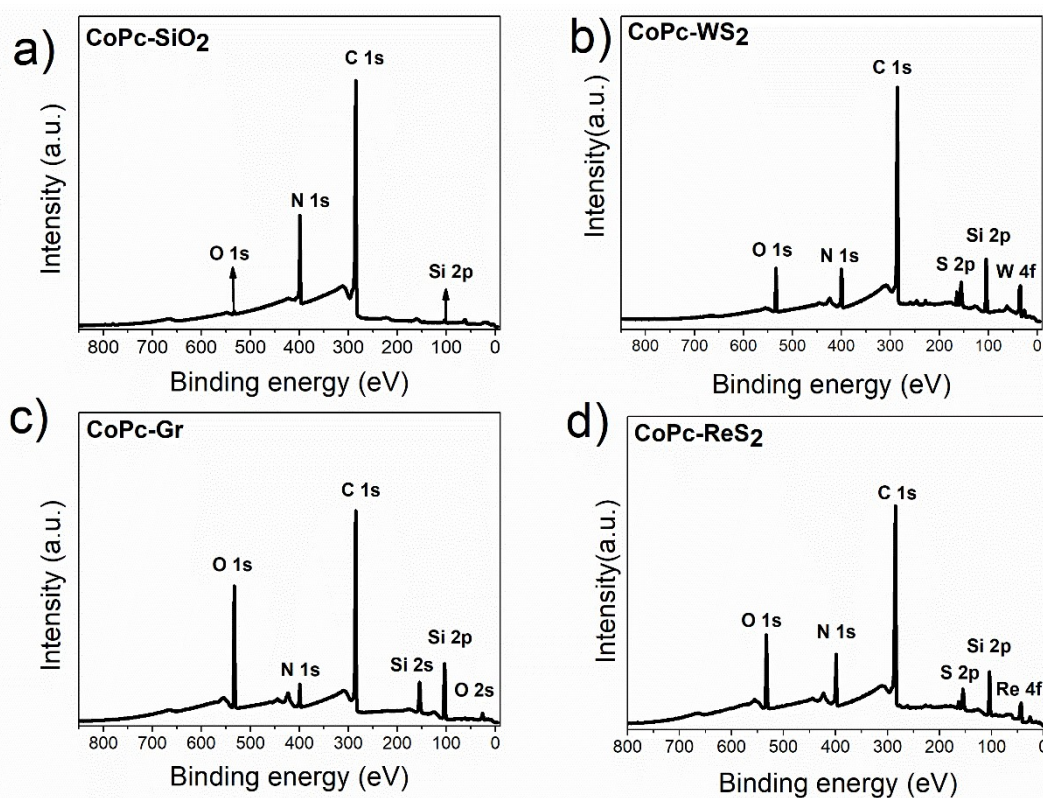


Fig. SI3. XPS survey spectra of CoPc films deposited on (a) SiO₂, (b) WS₂, (c) graphene (Gr), and (d) ReS₂ substrates. In each spectrum, the photoemission peaks corresponding to the main constituent elements are clearly identified. All survey spectra were acquired using a photon energy of 930 eV.

Determination of the molecular tilt angle from N K-edge NEXAFS

The molecular orientation of CoPc deposited on the 2D substrates was determined from polarization-dependent N K-edge NEXAFS spectra recorded at normal (90°) and grazing (15°) X-ray incidence with respect to the substrate surface. The synchrotron radiation was assumed to be linearly polarized in the plane of the storage ring. The resonance associated with the N 1s $\rightarrow \pi^*$ transition, centered at 398.3 eV, was used to estimate the average tilt angle (α) of the molecular π^* orbitals with respect to the surface normal. The tilt angle was obtained by fitting the angular dependence of the π^* resonance intensity according to the Stöhr equation:

$$I(\theta)=A[1+1/2(3\cos^2\alpha-1)(3\cos^2\theta-1)],$$

where $I(\theta)$ is the normalized π^* resonance intensity measured at the X-ray incidence angle θ (15° or 90°), and α is the average tilt angle between the π^* orbital axis and the surface normal. A is a proportionality constant related to the absorption cross-section.

Alternatively, when NEXAFS spectra are available only at two incidence angles, the tilt angle can be estimated from the intensity ratio $R=I(90^\circ)/I(15^\circ)$ using the simplified expression derived from the Stöhr formalism: ¹

$$R=2(1+\cos^2\alpha)/(2+\sin^2\alpha)$$

This approach provides a reliable estimate of the average molecular tilt based on the relative variation of the π^* resonance intensity between normal and grazing incidence.

The experimental spectra recorded at 90° and 15° were normalized to the post-edge region, and the fitting was performed only within the π^* resonance region (397–402 eV) to accurately determine the N 1s $\rightarrow \pi^*$ transition intensity. Each π^* feature was fitted using Gaussian functions, while the absorption edge step was modeled by an arctangent function to reproduce the overall spectral shape. The fitted spectra for the CoPc–Gr and CoPc–WS₂ samples are presented in Fig. SI1.

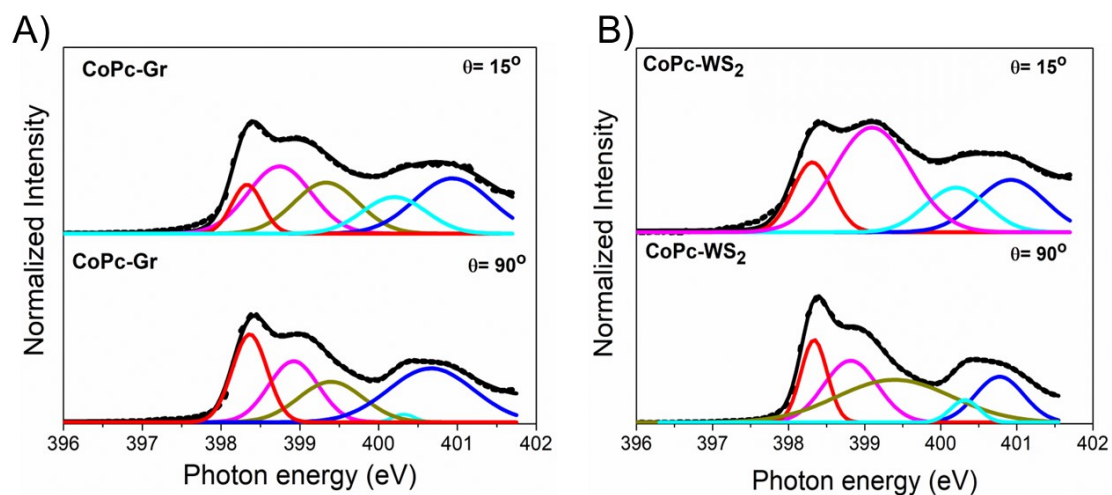


Fig. SI4. (a) Fitting of the N K-edge NEXAFS spectra collected at 15° and 90° for the CoPc–Gr sample. (b) Corresponding fitting of the spectra acquired at the same incidence angles for the CoPc–WS₂ sample.

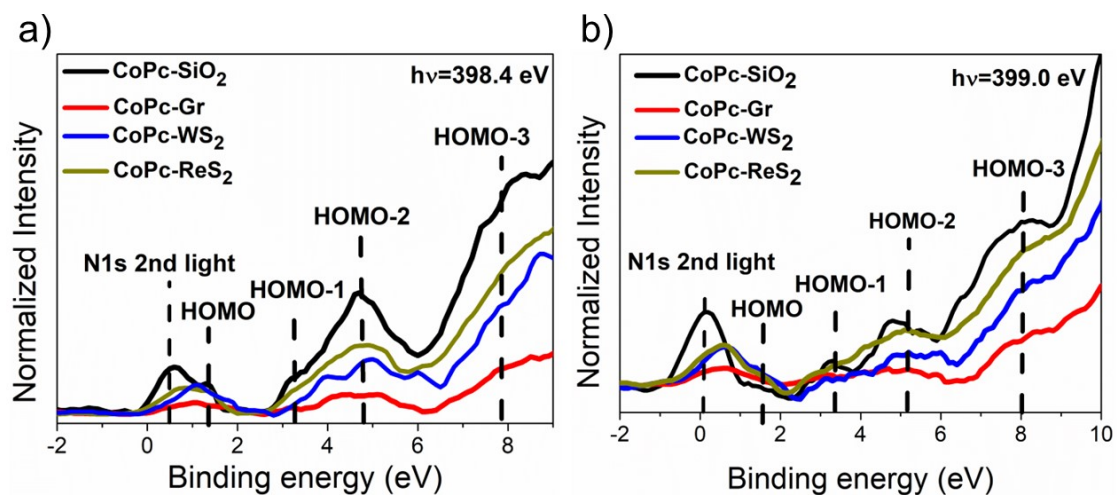


Fig. SI5. Resonant photoemission spectra (RPES) of CoPc deposited on SiO₂, graphene, WS₂, and ReS₂ substrates, recorded at excitation energies corresponding to the (a) N 1s → LUMO and (b) N 1s → LUMO+1 resonances. Each spectrum was obtained after subtraction of a pre-resonance spectrum to remove non-resonant background contributions.

Conversion and alignment of N K-edge NEXAFS Spectra

The N K-edge NEXAFS spectra were first converted from photon energy to binding energy (BE) referenced to the Fermi level. For this purpose, the excitation energy was subtracted from the N 1s ionization potential (IP) obtained from XPS measurements of the core level. To align the spectra relative to the conduction-band minimum (CBM) of each 2D substrate, the CBM position was determined as follows. The valence-band maximum (VBM) of the bare 2D substrates was extracted from the XPS valence-band spectra using a linear extrapolation method. Knowing the electronic band gap (E_g) of the 2D material, the CBM was then calculated as:

$$\text{CBM} = E_g - \text{VBM}.$$

For WS_2 and ReS_2 , E_g values of 2.0 eV² and 1.5 eV³, respectively, were used to determine the CBM position. Finally, the obtained CBM value was subtracted from the binding-energy scale of the NEXAFS spectra, resulting in N K-edge spectra aligned such that $\text{BE} = 0$ eV corresponds to the CBM of each 2D substrate. This procedure ensures a consistent energetic reference for direct comparison of molecular unoccupied states relative to the conduction-band edge of the substrates. The extrapolation procedure used to determine the VBM of WS_2 and ReS_2 is presented in Fig. SI6.

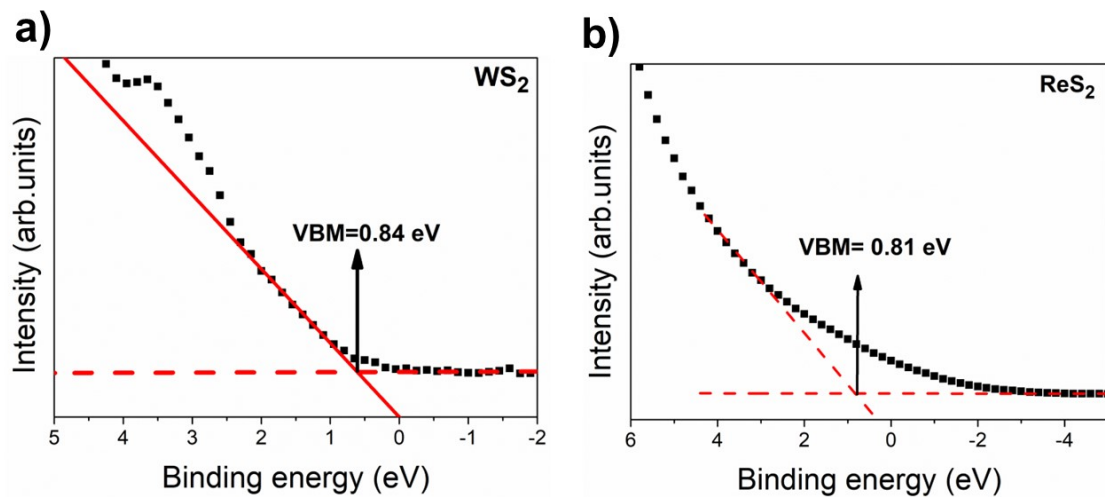


Fig. SI6. Valence band spectra of (a) WS_2 and (b) ReS_2 used to determine the valence band maximum (VBM) position. The VBM edge was extracted by linear extrapolation of the leading edge of the valence band to the baseline, allowing the estimation of the energy offset between the two 2D materials.

References

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