

Introduction

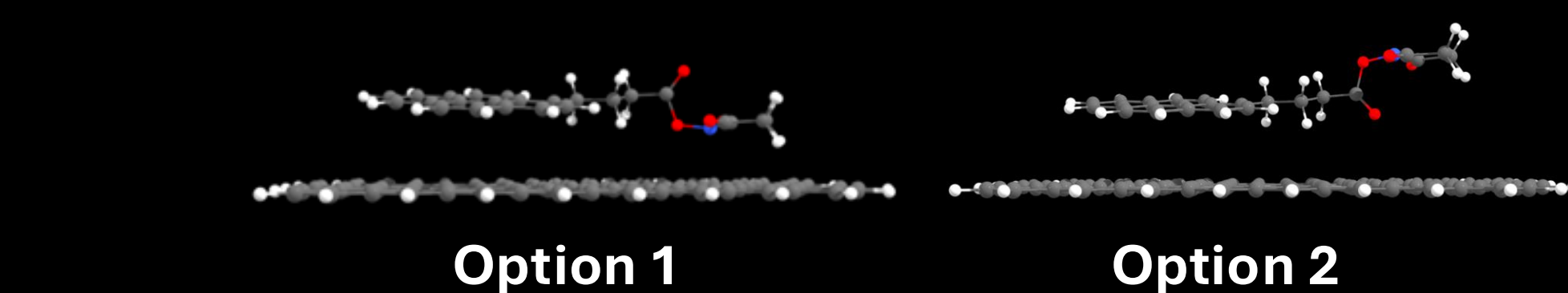
Micro- and nanoplastics are **pervasive pollutants** that evade routine monitoring [1,2]; graphene-supported, **π -conjugated sensor interfaces** offer a path to sensitive, selective, on-site detection [3–5]. **Quantum-chemical modelling** is used herein to evaluate two complementary probes for their capacity to transduce **polymer adsorption into measurable signals**.

The **plastic fragments used**:

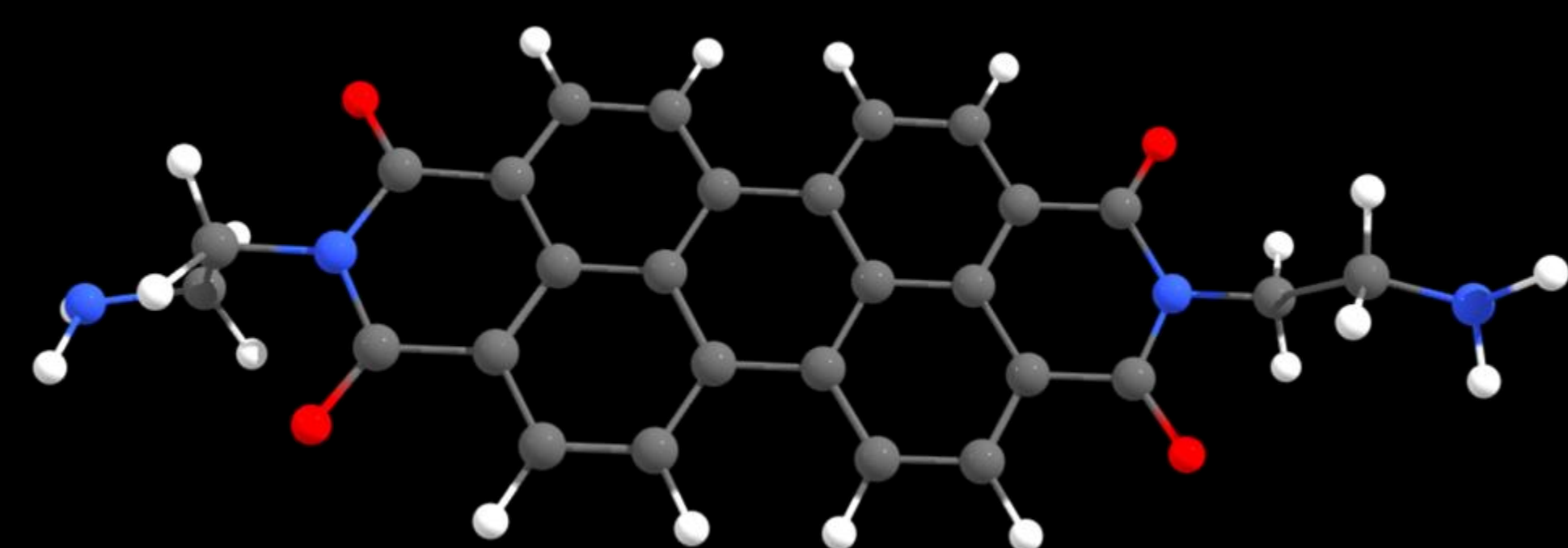
- Polyethylene (PE)
- Polypropylene (PP)
- Polyvinyl Chloride (PVC)
- Polyurethane (PU)
- Polyethylene terephthalate (PET)
- Polystyrene (PS)
- Nylon6

Sensors investigated herein:

- 1-Pyrenebutanoic Acid Succinimidyl Ester (PBASE)**
A pyrene-based, graphene-anchorable sensor interface evaluated in two configurations. **Option 1** has the lowest energy ($\Delta E = -3.3$ kcal mol⁻¹) and therefore used for subsequent calculations.



- Amphiphilic Perylene Diimide Probe (PDI-NH₂):**
An electrochemiluminescent (ECL) probe, sensitive to local environment; proximity of selected nanoplastic fragments can enhance signal via dispersion-driven complexation, microenvironment polarity, and charge-transfer effects.

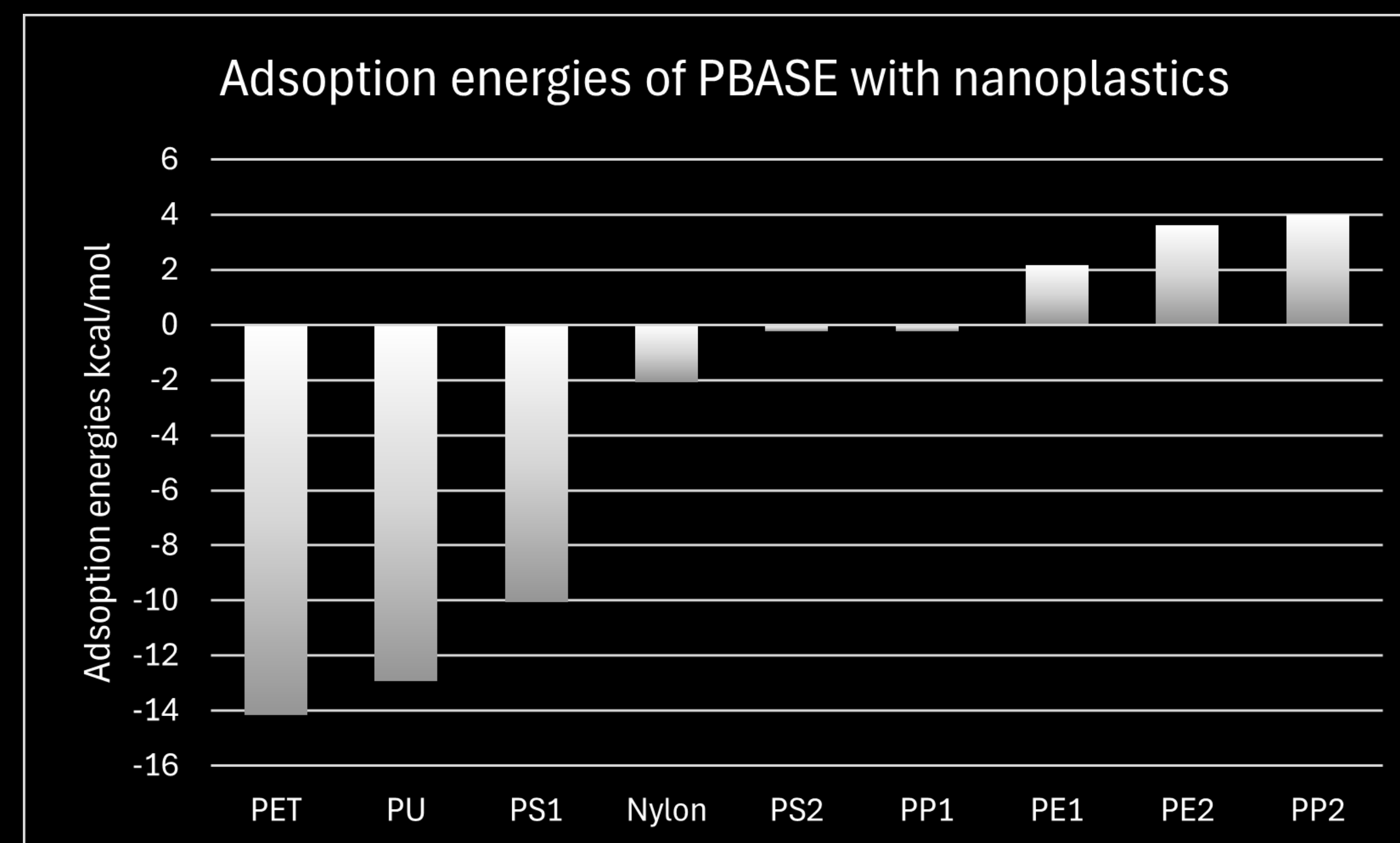
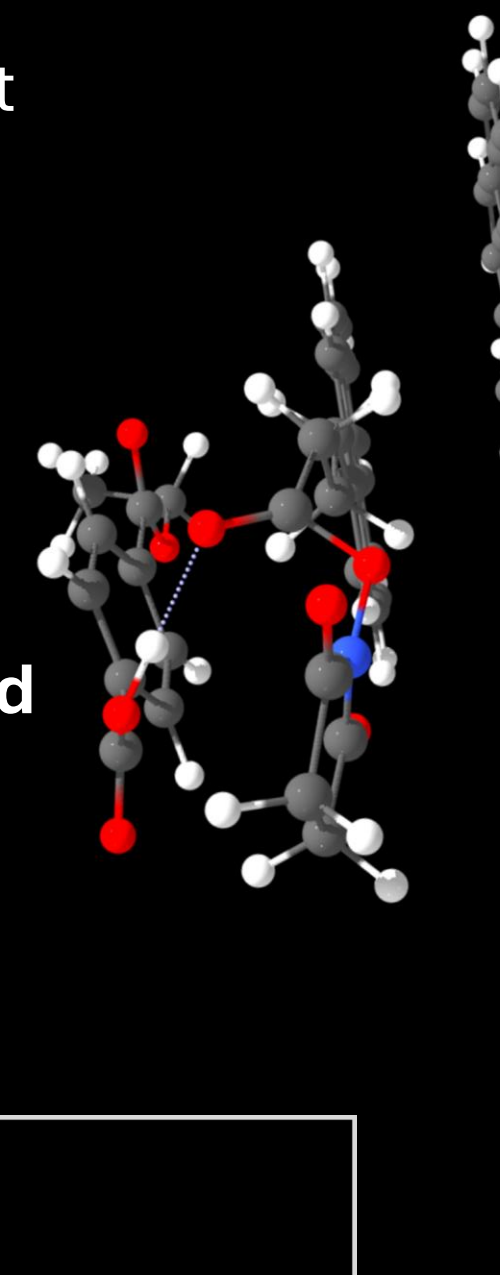


Methods

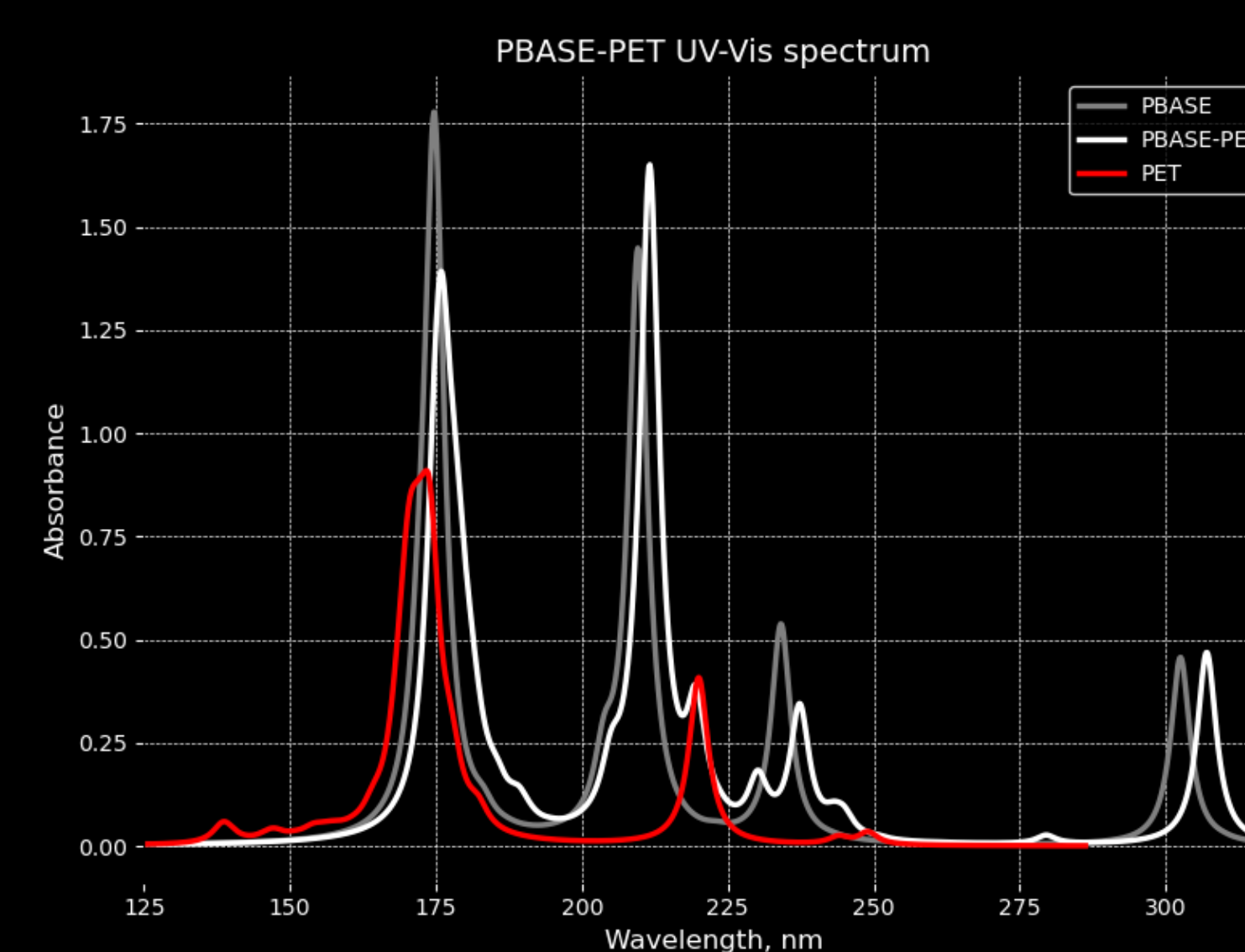
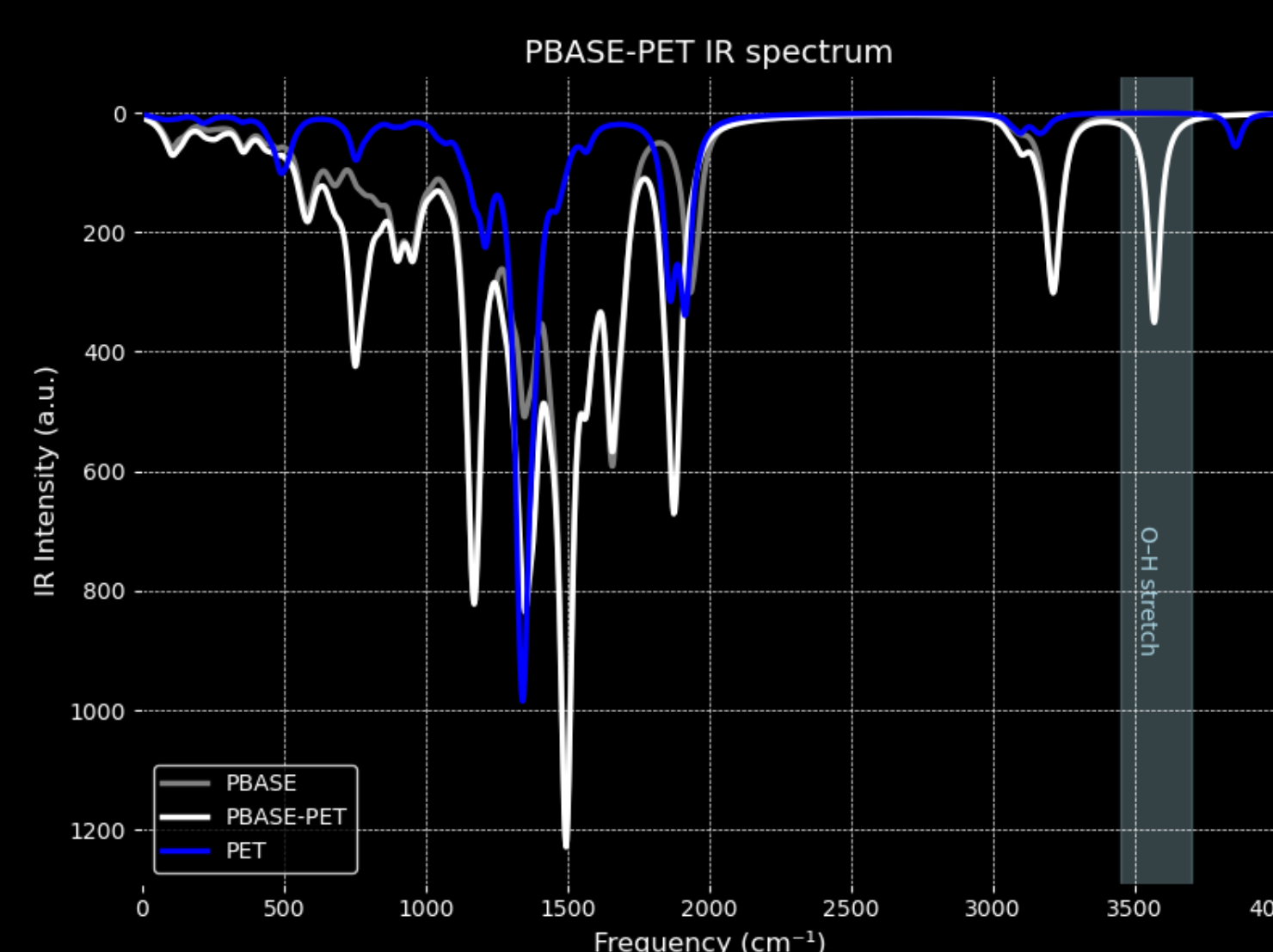
Biosensor–polymer assemblies were built and inspected in Chemcraft, then subjected to **DFT geometry optimisations** and harmonic frequency analyses in ORCA. Minima were verified by the absence of imaginary modes. **ZPE-corrected adsorption energies** were computed as the energy of the complex minus the sum of the isolated components at their optimised geometries. **IR spectra** were generated from the harmonic intensities and post-processed in Python. **Frontier** and **intrinsic bond orbitals** were visualised with IboView. **Vertical excited states** were obtained with TDDFT, and the corresponding simulated absorption profiles were plotted.

PBASE Results

- PBASE–PET** shows **strong adsorption** ($\Delta H = -14.16$ kcal mol⁻¹), consistent with a **directional H-bond** between the PET terminal –COOH and PBASE carbonyl/N–O sites, reinforced by π -contacts to the pyrene/graphene surface (right).
- PU** also **binds favourably** via urethane N–H...O/C=O interactions and dipolar coupling.
- Hydrocarbon-only fragments (PE, PP) exhibit **weak, dispersion-dominated physisorption** and often prefer the graphene support over the probe.
- PS engages in **π – π stacking** with **graphene**, yielding a comparatively **favourable adsorption energy** despite lacking strong specific H-bonding.

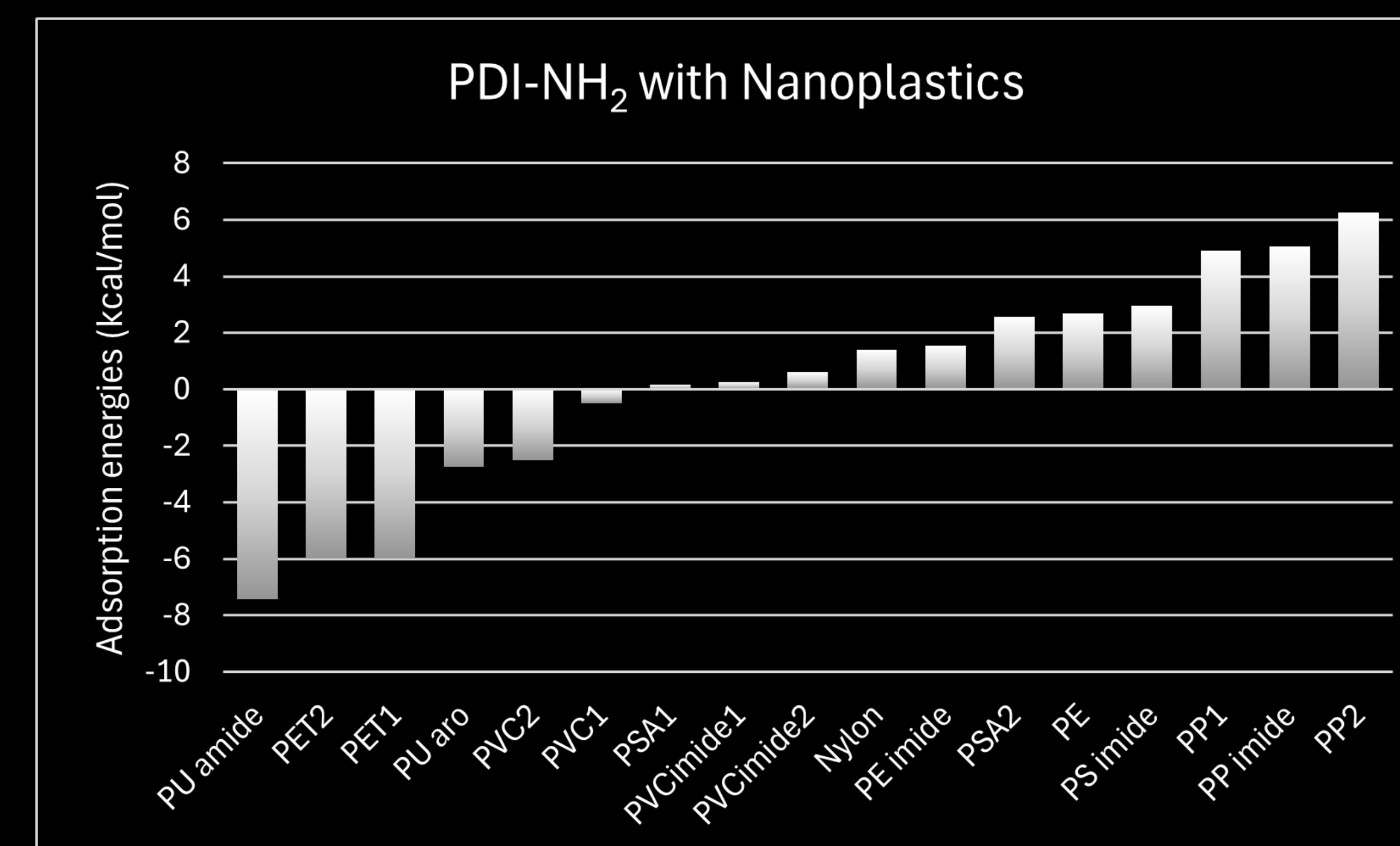


- IR signature.** An emergent band near **3500 cm⁻¹** is assigned to the **–OH stretch of PET** upon hydrogen bonding to the **PBASE**, diagnostic of a –COOH...C=O(PBASE) interaction.

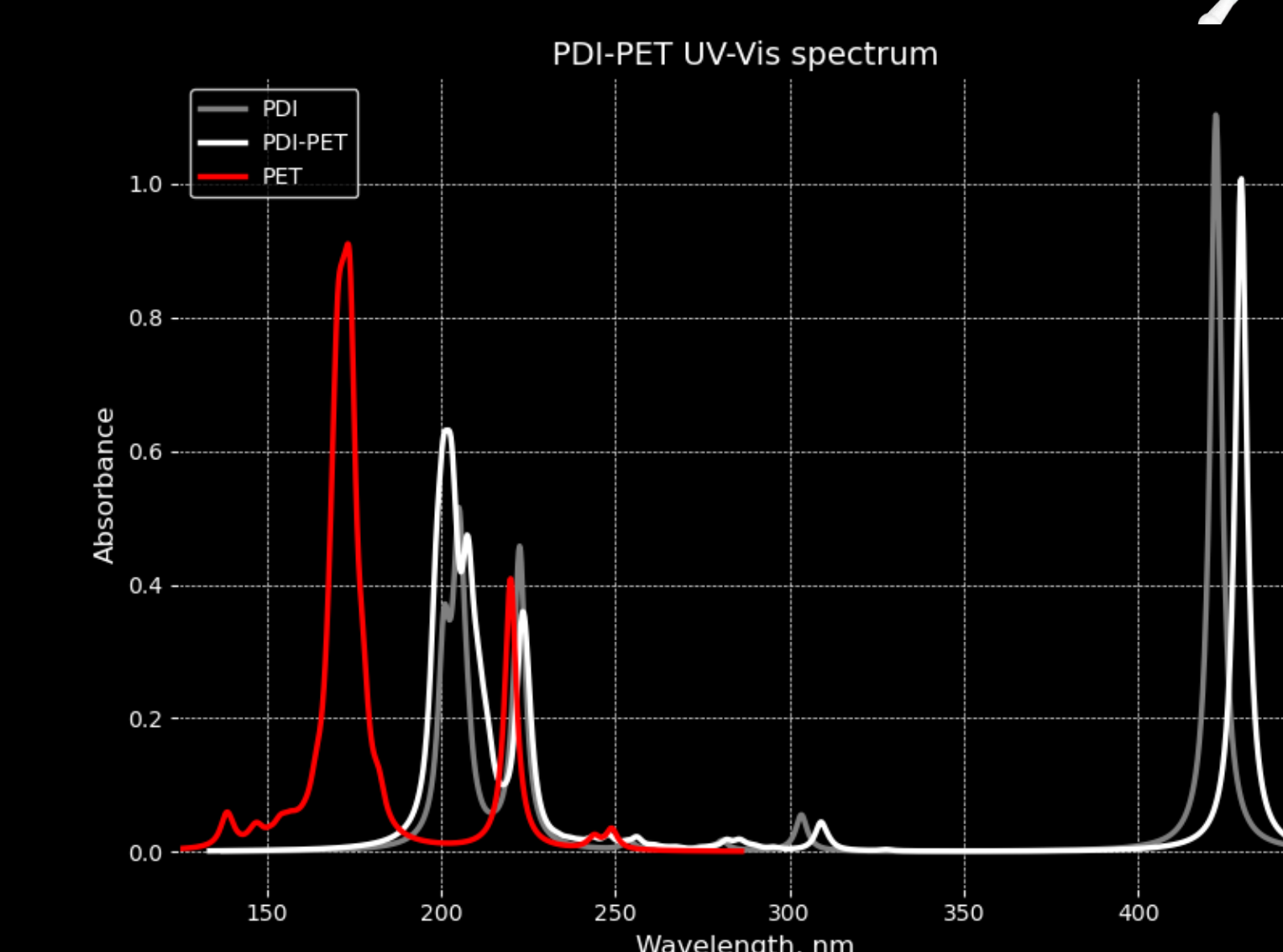
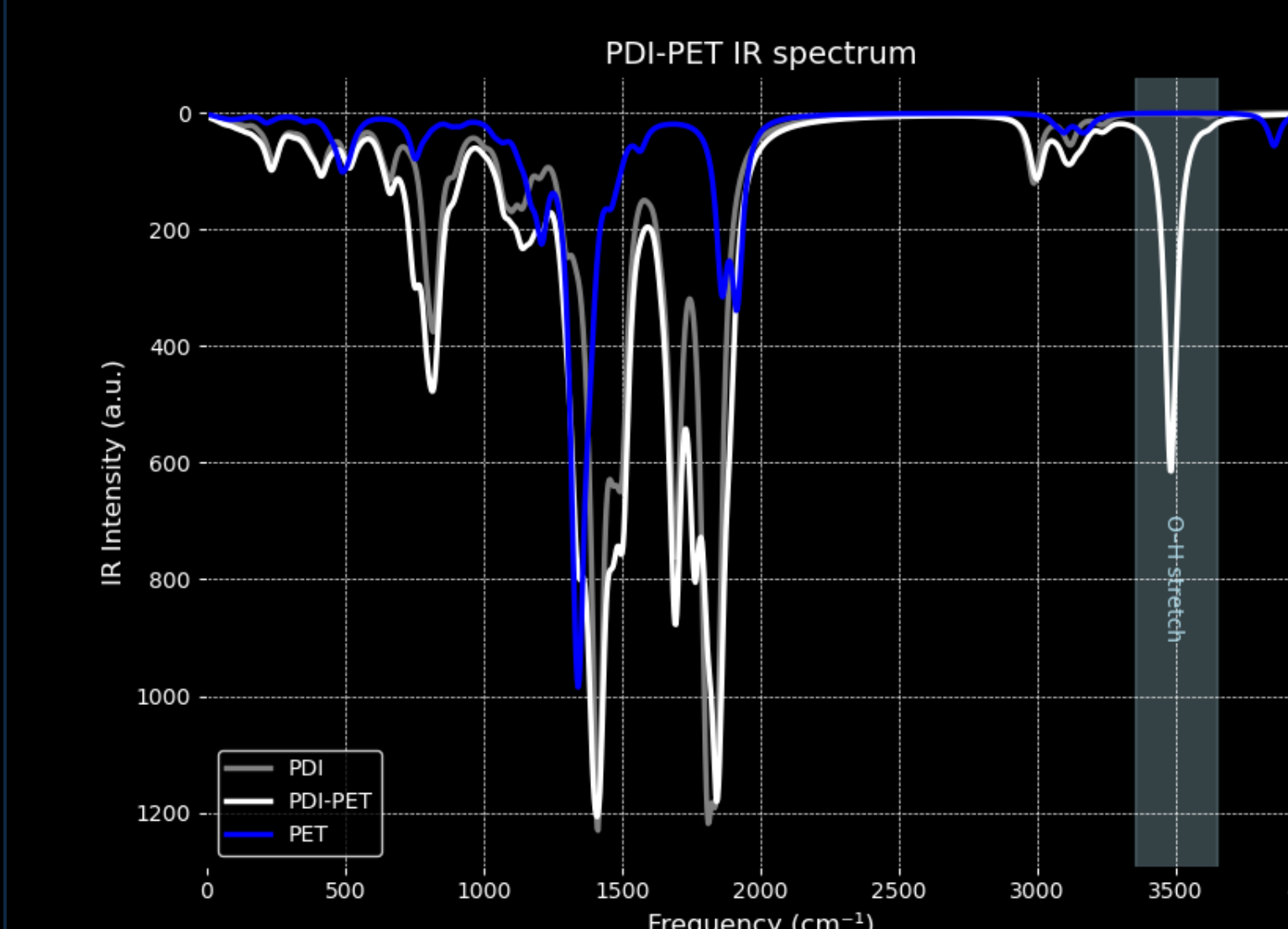
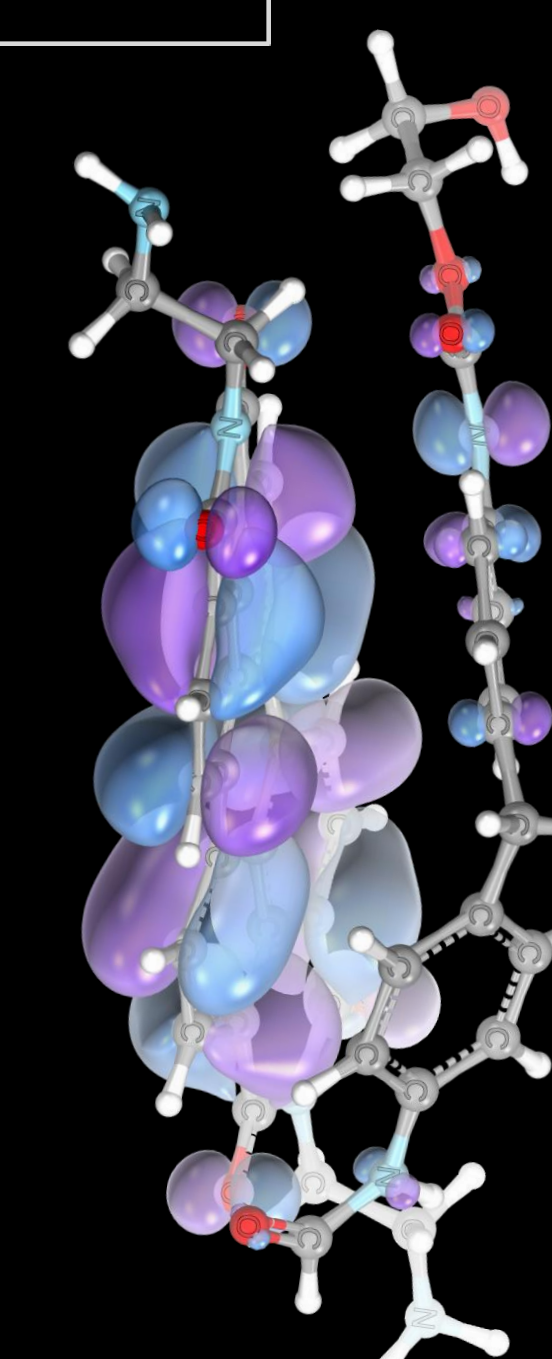


- UV-Vis response.** TDDFT predicts a **redshift**: the complex's lowest-energy transition occurs at **lower energy (longer wavelength)** than the isolated components. Together with the IR data, this supports **PBASE** as a **sensor for functionalised nanoplastics**.

PDI-NH2 Results



- PET** forms a **directional hydrogen bond** via its terminal –COOH to PDI-NH₂ (imide carbonyl/amine sites), giving favourable adsorption.
- PU** shows the **strongest binding**, consistent with complementary amide $\leftrightarrow$ imide H-bonding and π – π contacts between aromatic segments and the perylene core; the HOMO is delocalised across the interface (right).
- By contrast, **hydrocarbon nanoplastics** (PE, PP) do not seem to exhibit strong binding to PDI-NH₂, showing mainly weak, dispersion-dominated contacts.
- A recent study [5] reported strong PP–PDI-NH₂ binding with enhanced ECL signal. Our model predicts weak adsorption for neutral, unoxidised PP fragments; the difference may reflect surface oxidation/functionalisation of PP, probe protonation/ionic strength, solvent effects, or particle size/curvature not captured in idealised fragment models.



Spectroscopic response. A hydrogen-bond signature appears near 3500 cm⁻¹ with **greater intensity than PBASE**, consistent with stronger/more numerous H-bond contacts. The UV-Vis profile is largely conserved; only the highest-energy band shows a slight **redshift**, as with PBASE, indicating **modest but distinct electronic coupling**.

Conclusions

- PBASE shows more favourable (ZPE-corrected) adsorption energies than PDI-NH₂, indicating stronger interfacial capture on graphene.
- PET/PU bind strongly via directional H-bonding and dipolar contacts; PE/PP are weak, often preferring the graphene support; PS engages π – π stacking with graphene, giving moderate binding.
- A new ~3500 cm⁻¹ IR band marks H-bond formation (typically more intense for PDI-NH₂). TDDFT indicates small redshifts in the highest-energy UV-Vis band, consistent with modest electronic coupling.
- Affinity increases with available donors/acceptors (–COOH, amide) and aromatic surface area; graphene anchoring with π -rich probes prolongs residence time and improves transduction.
- PBASE is the more robust general interface; both probes are best suited to functionalised nanoplastics (e.g., PET, PU) rather than purely hydrocarbon fragments.
- Next steps: Add explicit solvent, test larger and/or oxidised fragments and curvature, and validate via experiments.

References

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