

Supporting Information for

Controlling the Charge Transfer Flow at the Graphene/Pyrene- Nitrilotriacetic Acid Interface

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Table S1. Relevant bond distances obtained after geometry optimization at the DFTB level of theory. All distances are in Å.

	C=C (sp ²)	C-C (sp ³)	C=O	C-N	C=(O)-OH	C=O-(OH)
pyrNTA/G	1.43	1.52	1.23	1.37/1.45	1.39	1.22
	Ni-O	Ni-N(Imid)	Ni=O	Ni-N (NTA)	C=C (sp ²)	
pyrNTA-Ni-IM/G	1.87/1.89	2.02	2.91	2.98	1.43	

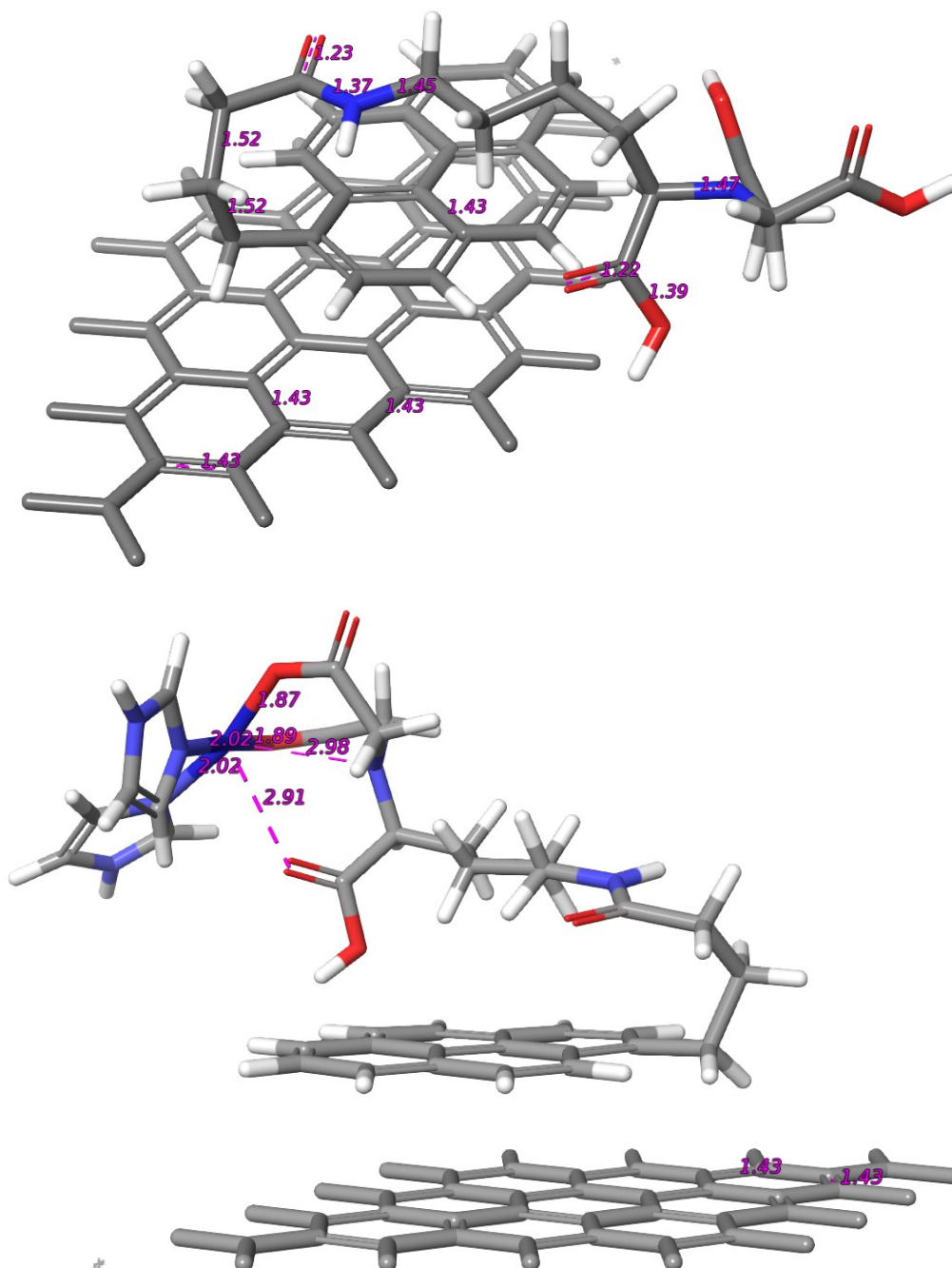


Figure S1. Optimized geometries for the pyrNTA/G (top) and pyrNTA-Ni-IM/G (bottom) interfaces. Significant bond distances are reported.

A second orientation of pyrNTA on graphene has been found from theoretical calculation, and is here reported (hereafter mentioned as pyrNTA₂/G). The absorption energy for this system has been calculated to be -0.34 eV, slightly lower than for the pyrNTA/G interface.

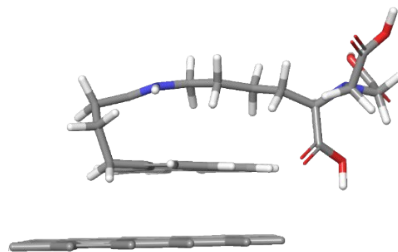


Figure S2. Second conformer of pyrNTA found from theoretical optimization of the structure.

In comparison with pyrNTA, this new interface has slightly longer minimum distance of 2.96 Å between pyrene/graphene, and a ‘distorted’ Bernal-stacking pattern. In addition, the orientation of the carboxylic groups of NTA strongly differs. Yet, the impact in the WF shift is minimal (see Figure S3).

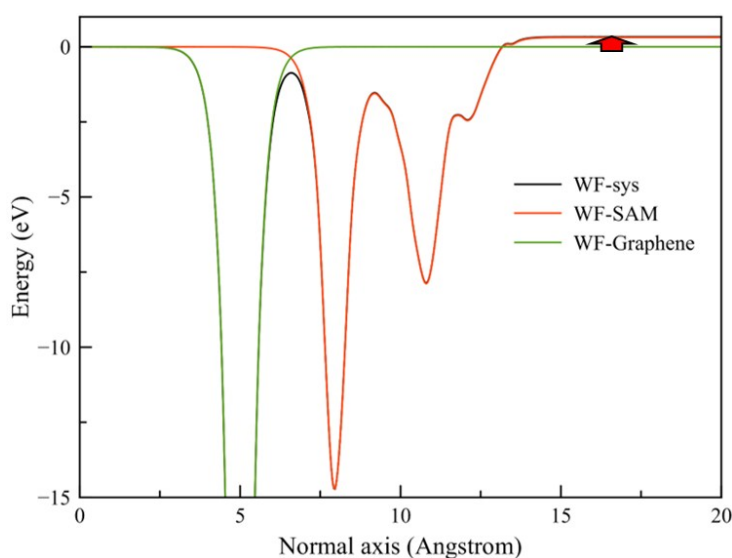


Figure S3. Plane averaged potential of the G/pyrNTA₂ interface. The displayed curves refer to the bare graphene monolayer (green), the graphene surface covered by SAM (black) and the free SAM layer (red). Going from left to right, we move from the graphene surface to the SAM contribution, away from the surface. The red thick arrow indicates the total work function shift of the G/SAM interface. The difference between this shift and the SAM contribution corresponds to the charge transfer.

The WF shift of 0.33 eV is similar to the pyrNTA system (of 0.42 eV), thus validating the observation that small changes in conformation do not have a strong impact on the WF shift. Interestingly, also

the SAM contribution has similar value of 0.31 eV, while the CT contribution of 0.02 eV is lower which, in turn, reflect the negligible CT contribution of 0.001 |e| (Figure S3).

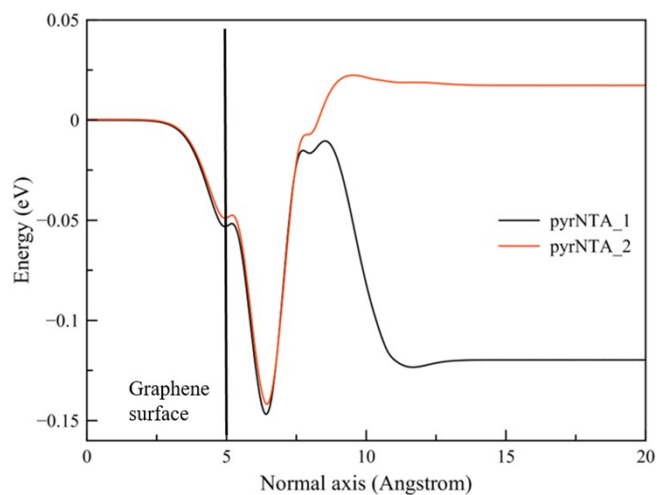


Figure S4. Evolution of the charge transfer contribution to the work function. From left to right we move away from the graphene surface (indicated as a black bar) towards the SAM layer. For both systems investigated, the $\Delta\Phi_{CT}$ contribution increases up to the end of the molecular backbone.

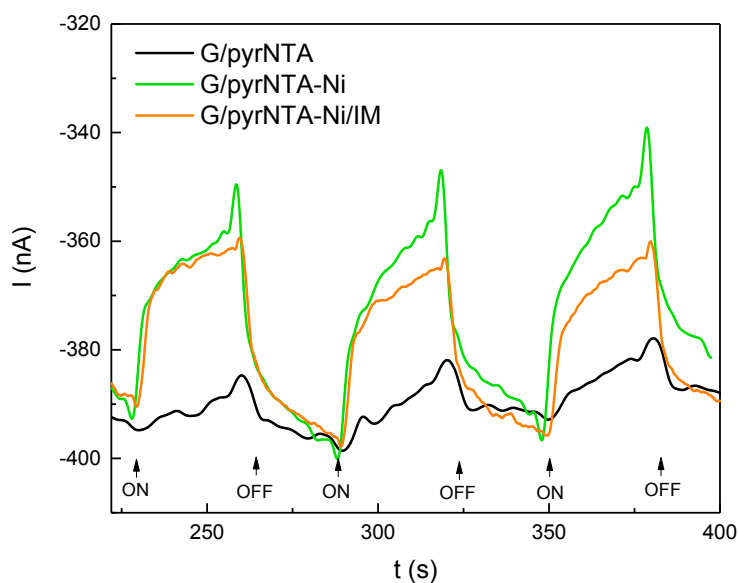


Figure S5. Photochronoamperometric analysis of FTO/graphene electrodes. Shown are the representative photochronoamperograms for three modified systems: pyrene-NTA moiety on graphene (G/pyrNTA), graphene/pyrene-NTA layer with Ni²⁺ cations (G/pyrNTA-Ni) and graphene/pyrene-NTA-Ni layer coordinated with imidazole (G/pyrNTA-Ni-IM). Measurements were recorded at a -200 mV overpotential with 30-s. illumination cycles.