Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Title: Theoretical Study of the Adsorption of Analgesic Environmental Pollutants on Pristine and Nitrogen-Doped Graphene Nanosheets

Authors: Richard H. Perry*

Affiliation: Department of Chemistry and Physics, Nova Southeastern University, Fort Lauderdale, FL 33314

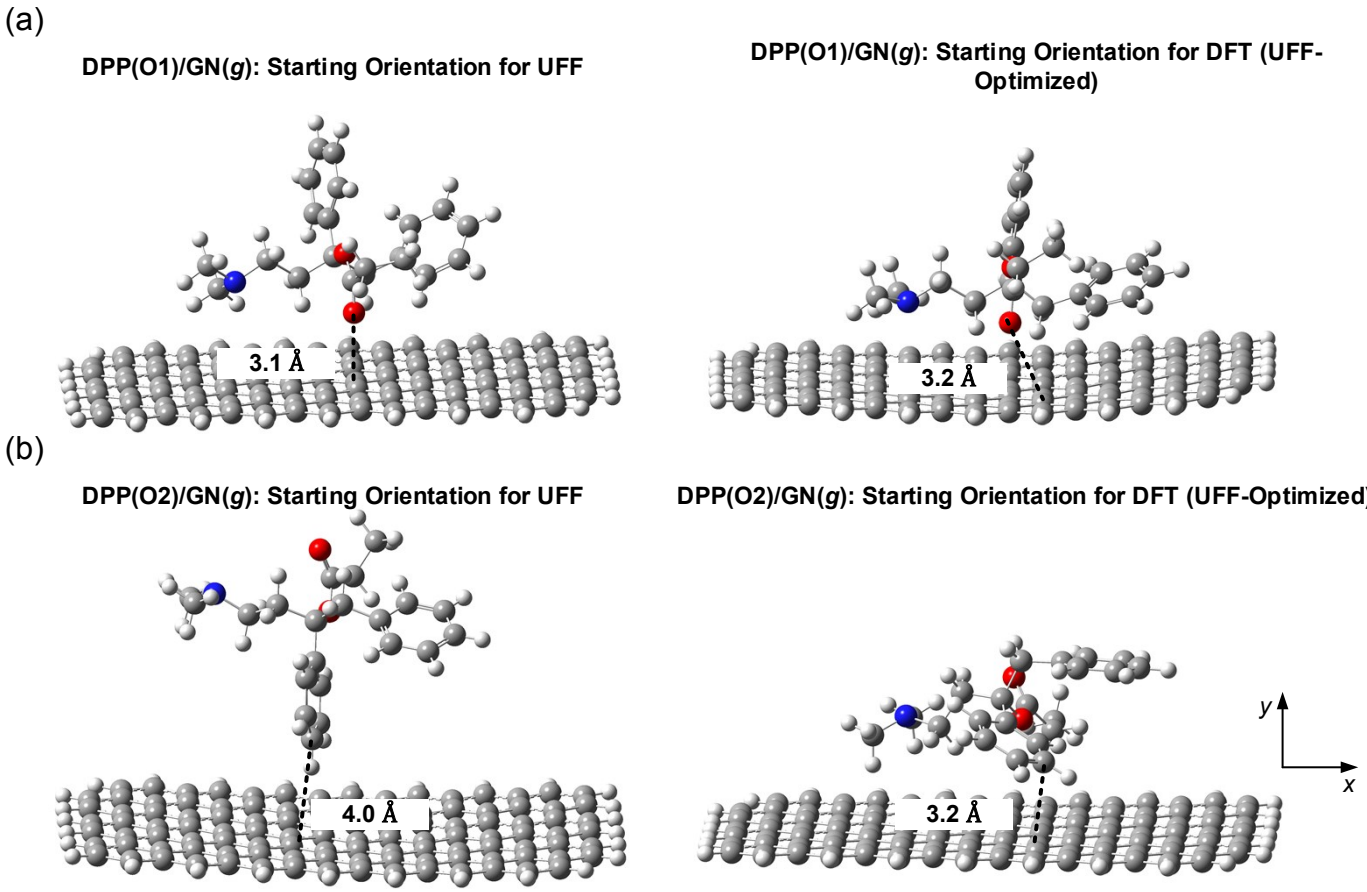

Figure S1. (a) DPP(O1)/GN(g) and (b) DPP(O2)/GN(g) starting orientations for calculations using the Universal Force Field (UFF) (left column) and Density Functional Theory (DFT) (right column). The starting orientation for DFT calculations were obtained from UFF geometry optimizations. (Atom colors: carbon (grey), hydrogen (white), oxygen (red), nitrogen (blue)).

Table S1. Vibrational frequency modes for each analgesic/nanosheet complex in the aqueous and gas phases. The lowest calculated

frequency mode is designated f_L. The three most intense frequency modes are designated f_1, f_2, and f_3, in order of decreasing intensity (viz. $f_1 > f_2 > f_3$).

Complex	Gas Phase				Aqueous Phase			
	f_L (cm^{-1})	f_1 (cm^{-1})	f_2 (cm^{-1})	f_3 (cm^{-1})	f_L (cm^{-1})	f_1 (cm^{-1})	f_2 (cm^{-1})	f_3 (cm^{-1})
GN	11.63	899.39	1447.55	1219.34	11.78	140.36	1444.84	1216.84
DPP(O1)/GN	4.32	1448.09	1219.74	898.51	7.65	141.20	1445.48	1567.27
DPP(O2)/GN	10.61	1220.09	1448.23	899.49	10.76	1445.53	1567.78	1217.59
PCL(O1)/GN	10.94	296.43	1219.87	1448.13	10.92	140.40	1217.55	1445.56
PCL(O2)/GN	10.66	296.24	1448.55	1219.84	11.89	140.68	1445.53	1567.44
TDL(O1)/GN	10.96	1219.84	1447.68	142.58	9.53	140.60	1217.19	1445.21
TDL(O2)/GN	11.06	1448.24	1220.27	1570.12	11.70	140.70	1445.44	1217.80
IBN(O1)/GN	10.15	1448.12	1219.83	899.43	10.76	140.58	1445.29	1567.36
IBN(O2)/GN	10.99	899.42	1219.79	1448.04	4.45	140.53	1445.29	1217.38
NPX(O1)/GN	9.90	1220.31	1448.33	142.94	10.43	140.49	1217.90	1445.66
NPX(O2)/GN	10.96	1448.46	1220.20	143.01	3.43	3.43	140.36	1567.87
NGN	3.92	1004.47	800.67	1335.98	4.56	797.97	992.85	980.57
DPP(O1)/NGN	6.50	1006.89	1150.83	1318.33	6.62	993.05	1329.71	1075.83
PCL(O2)/NGN	9.03	1367.65	1007.07	1581.85	7.11	971.69	788.32	1141.72
TDL(O1)/NGN	8.04	1599.61	809.45	1319.54	7.22	995.27	981.77	1330.88
IBN(O2)/NGN	4.02	812.30	1007.07	1337.35	5.10	799.38	993.64	983.94
NPX(O2)/NGN	4.98	798.24	1005.66	1336.86	5.93	979.90	795.61	1330.73

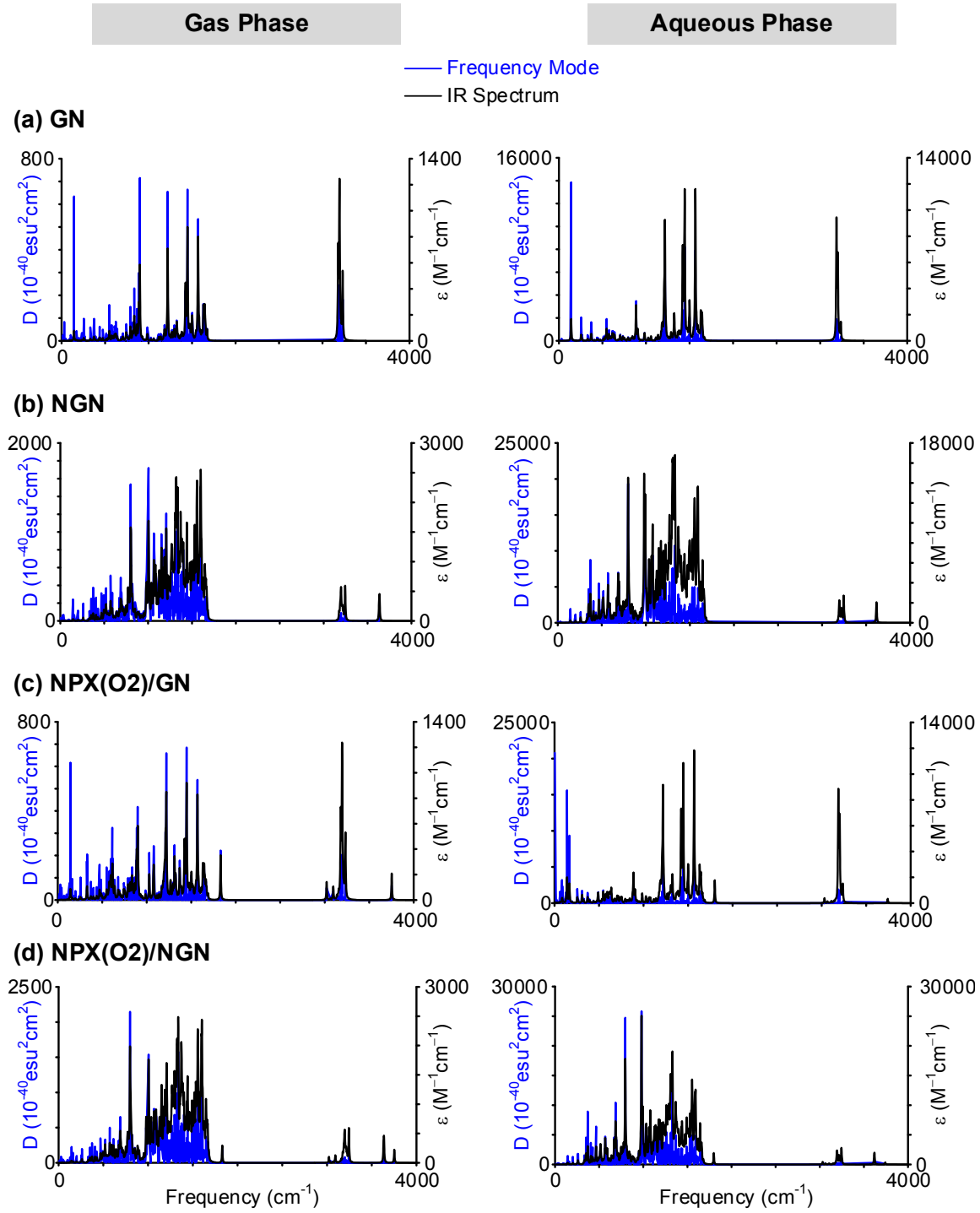

Figure S2. Calculated vibrational frequency modes and infrared spectra for (a) GN, (b) NGN, (c) NPX(O2)/GN, and (d) NPX(O2)/NGN in the gas and aqueous phases.

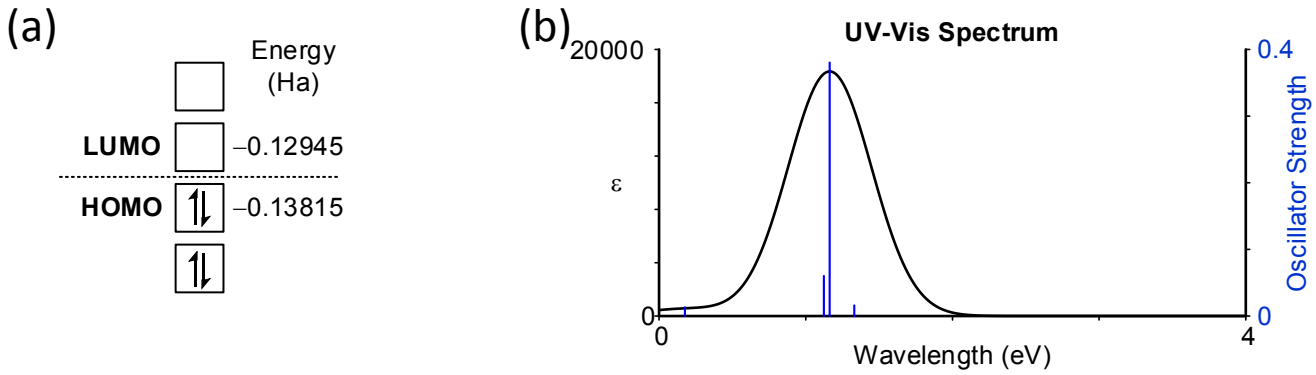

Figure S3. (a) Energies of the HOMO and LUMO for GN(*g*). HOMO = –3.76 eV, LUMO = –3.52 eV, HOMO-LUMO Gap = 0.24 eV. (b) Calculated UV-Vis spectrum for GN(*g*) obtained through time-dependent DFT (TD-DFT). The lowest excitation occurs at 0.17 eV with oscillator strength of 0.013 (specific excitation wavelengths are shown as blue lines). Based on these results, the calculated work function for GN(*g*) = | –3.76 + 0.17 | = 3.59 eV.

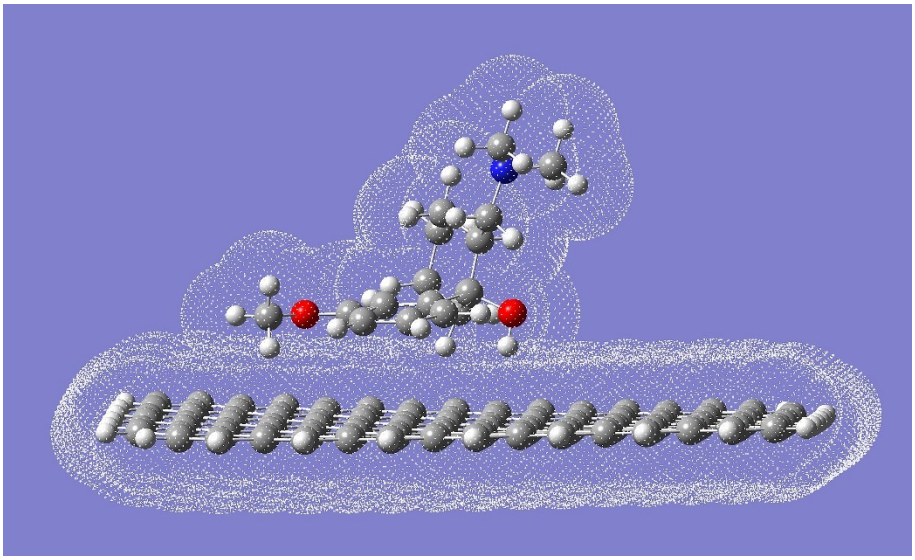

Figure S4. Geometry-optimized structure for TDL(O1)/GN(*aq*) showing the solvent cavity (small white dots represent water molecules; carbon (grey spheres); hydrogen (white spheres); oxygen (red spheres); nitrogen (blue spheres)).

Table S2. Electronic properties of analgesic/nanosheet complexes in the gas phase.

Complex	Gas Phase				
	HOMO (eV)	LUMO (eV)	HOMO-LUMO Gap (eV)	Lowest Energy Excitation (eV)	Work Function (eV)
DPP(O1)/GN	−3.71	−3.48	0.24	0.17	3.54
DPP(O2)/GN	−3.81	−3.58	0.24	0.17	3.64
PCL(O1)/GN	−3.78	−3.55	0.24	0.16	3.62
PCL(O2)/GN	−3.78	−3.54	0.24	0.18	3.60
TDL(O1)/GN	−3.79	−3.55	0.24	0.17	3.62
TDL(O2)/GN	−3.76	−3.53	0.24	0.18	3.59
IBN(O1)/GN	−3.76	−3.52	0.24	0.18	3.58
IBN(O2)/GN	−3.76	−3.52	0.24	0.17	3.59
NPX(O1)/GN	−3.75	−3.51	0.24	0.17	3.57
NPX(O2)/GN	−3.76	−3.52	0.24	0.18	3.58
DPP(O1)/NGN	−2.67	−2.05	0.63	0.17	2.50
PCL(O2)/NGN	−2.71	−2.12	0.59	0.12	2.58
TDL(O1)/NGN	−2.69	−2.07	0.63	0.18	2.52
IBN(O2)/NGN	−2.70	−2.06	0.64	0.19	2.51
NPX(O2)/NGN	−2.69	−2.09	0.61	0.17	2.53

Table S3. Electronic properties of analgesic/nanosheet complexes in the aqueous phase.

Complex	Aqueous Phase				
	HOMO (eV)	LUMO (eV)	HOMO-LUMO Gap (eV)	Lowest Energy Excitation (eV)	Work Function (eV)
DPP(O1)/GN	−3.88	−3.64	0.24	0.16	3.71
DPP(O2)/GN	−3.90	−3.67	0.24	0.16	3.74
PCL(O1)/GN	−3.89	−3.65	0.24	0.16	3.72
PCL(O2)/GN	−3.88	−3.64	0.24	0.16	3.72
TDL(O1)/GN	−3.90	−3.66	0.24	0.16	3.73
TDL(O2)/GN	−3.89	−3.66	0.24	0.16	3.73
IBN(O1)/GN	−3.90	−3.67	0.24	0.16	3.74
IBN(O2)/GN	−3.90	−3.67	0.24	0.16	3.74
NPX(O1)/GN	−3.88	−3.64	0.24	0.16	3.71
NPX(O2)/GN	−3.88	−3.64	0.24	0.17	3.71
DPP(O1)/NGN	−2.82	−2.18	0.64	0.19	2.63
PCL(O2)/NGN	−2.81	−2.20	0.61	0.14	2.67
TDL(O1)/NGN	−2.84	−2.18	0.66	0.19	2.65
IBN(O2)/NGN	−2.86	−2.21	0.65	0.20	2.65
NPX(O2)/NGN	−2.81	−2.19	0.62	0.18	2.63