Theoretical Investigation of Electrochemical Behavior of DTPA and Its Interfacial Synergy with Defected Graphene toward Photocatalytic Applications

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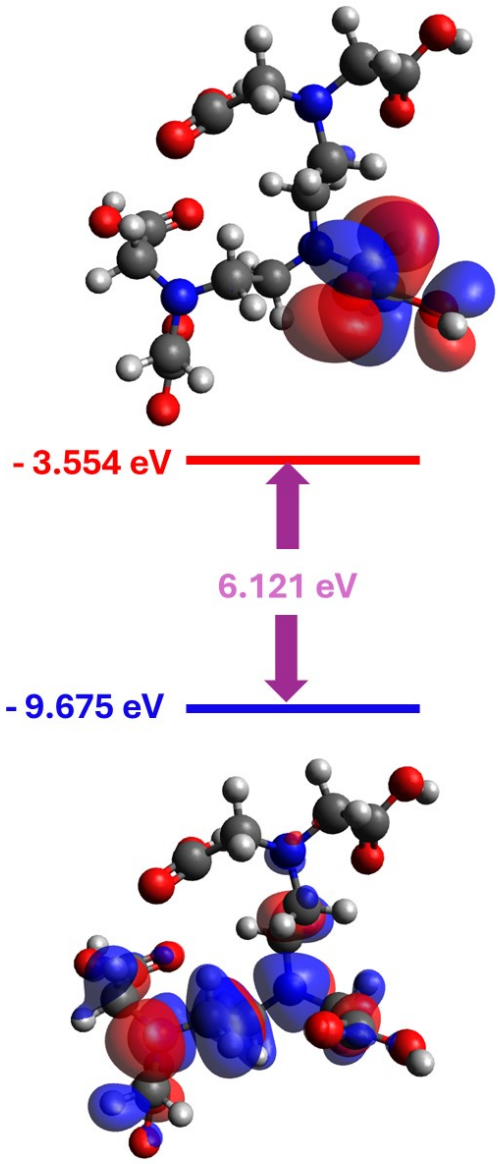

Figure S1. Calculated frontier orbital energies (SOMO and LUMO) and SOMO–LUMO gap of the DTPA molecule in radical cationic state.

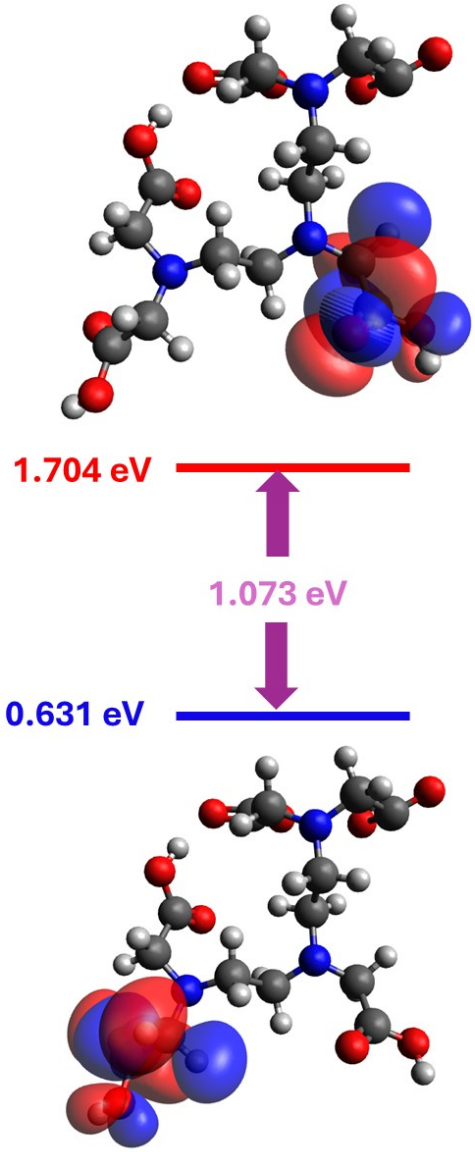

Figure S2. Calculated frontier orbital energies (SOMO and LUMO) and SOMO–LUMO gap of the DTPA molecule in radical anionic state.

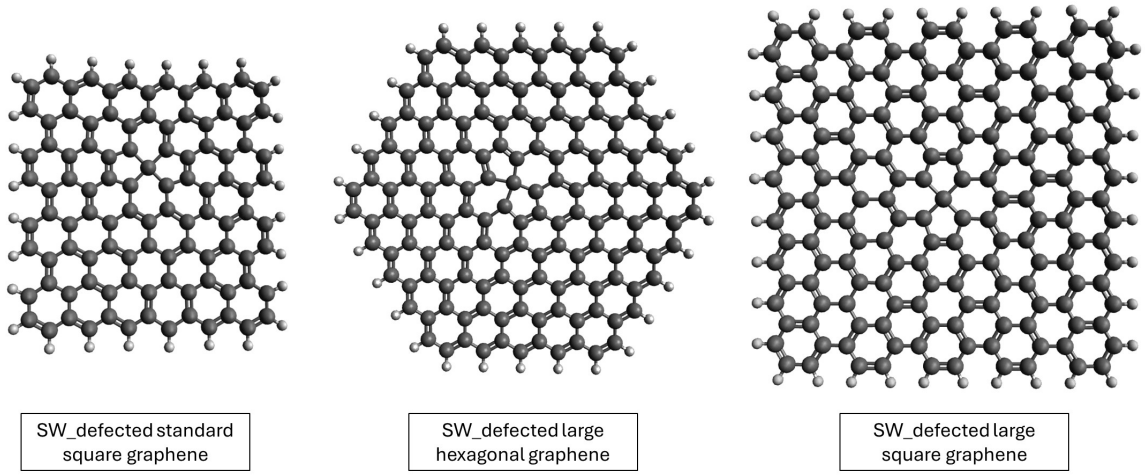

Figure S3. Finite graphene cluster models used for the convergence tests

Table S1. Spin expectation values $\langle S^2 \rangle$ for neutral and charged states of DTPA.

State	Multiplicity	Ideal $\langle S^2 \rangle$	Calculated $\langle S^2 \rangle$	Deviation (%)
Neutral	Singlet	0.00	0.00	0.0
Cation+1	Doublet	0.75	0.76	1.3
Cation+2	Singlet	0.00	0.00	0.0
Cation+3	Doublet	0.75	0.78	4.0
Anion−1	Doublet	0.75	0.76	1.3
Anion−2	Singlet	0.00	0.00	0.0
Anion−3	Doublet	0.75	0.80	6.7

Table S2. CPCM solvation parameters for DTPA in water, ethanol, DMF, and acetonitrile, accompanied by the corresponding single point energies

	Single Point Energy (eV)	**CPCM parameter**			
		Surface charge (eV)	**Outlying charge correction (eV)**	**Cavitation+ dispersion (eV) ***	**Dielectric interaction (eV)**
vacuum	-39832.0714	—	—	—	—
water	-39833.7786	-0.07985	0.00891	0.45851	-2.9632
EtOH	-39833.7875	-0.06253	0.00524	0.29406	-2.66705
DMF	-39833.6076	-0.01768	0.00038	-0.44443	-1.40447
ACN	-39833.5344	-0.02058	0.00053	-0.20213	-1.62183

Note: * - The sign of the cavitation + dispersion term depends on whether cavitation (positive) or dispersion attraction (negative) dominates for the given solute–solvent pair.

Table S3. Static electric properties of DTPA in vacuum and various solvents (water, ethanol, DMF, acetonitrile).

	Static Polarizability Tensor (a.u.)		**Quadrupole Moment (a.u.)**	**Dipole Moment (Debye)**
	Quad./Quad.	Dipole/Dipole		
vacuum	11849	221.04973	-118.949006	4.7923
water	15980	307.33502	-120.386379	7.9635
EtOH	15536	302.20891	-119.972433	7.6762
DMF	14607	289.32835	-119.713746	6.8565
ACN	14774	292.1804	-119.561643	7.0384

Table S4. Calculated Proton Affinity (PA) and neutralization energy for DTPA anionic states in aqueous phase.

Protonation Process	ΔG_{solv} (kcal/mol)	ΔG_{solv} (eV)	Tendency for PCET
Anion-1 + H^+ → Neutral	-285.4	-12.37	Moderate
Anion-2 + H^+ → Anion-1-H	-352.1	-15.27	High
Anion-3 + H^+ → Anion-2-H	-418.6	-18.15	Very High

Note: PA values are calculated as the Gibbs free energy change of the protonation step in water. Higher absolute values indicate a stronger thermodynamic driving force for capturing a proton.

Table S5. Static electric parameters and relative single point energies of DTPA anion and cation in water environment with respect to the neutral molecule.

	Dipole Moment (Debye)	**Single Point Energy (eV)**	**CPCM parameter**			
			Surface charge (eV)	Outlying charge correction (eV)	Cavitation+ dispersion (eV)	Dielectric interaction (eV)
Anion	16.357	-1.5078	0.9883	0.0028	-0.069	-1.888
Cation	7.463	5.0409	-0.99	-0.002	0.0647	-1.832

Table S6. Spin expectation values $\langle S^2 \rangle$ for neutral and charged states of materials.

System	Multiplicity	$\langle S^2 \rangle$	Magnetic moment* (μB)	Spin state
Pristine graphene	Singlet	0.00	0.00	Non-magnetic
SW_graphene	Singlet	0.00	0.00	Non-magnetic
V_1-graphene	Triplet	2.02	2.00	Magnetic (S=1)
V_1-graphene + DTPA	Singlet	0.00	0.00	Quenched
SW_graphene + DTPA	Singlet	0.00	0.00	Non-magnetic
Pris_graphene + DTPA	Singlet	0.00	0.00	Non-magnetic

Note: * - The magnetic moment (μB) is derived from the integrated spin density

The isolated single-vacancy defect (V_1-*) exhibits a triplet ground state with a magnetic moment of 2.00 μB, consistent with previous theoretical studies (Palacios et al., Vacancy-induced magnetism in graphene and graphene ribbons, Phys. Rev. B 2008). Upon adsorption of DTPA, the magnetic moment is completely quenched due to charge transfer and orbital hybridization between the vacancy site and the DTPA molecule. No spin contamination is observed ($\langle S^2 \rangle$ values are within 0.02 of the ideal). The SW and pristine models remain non-magnetic throughout.*

Table S7. Convergence of Adsorption Energy and Electronic Properties for DTPA on SW-Defected Graphene Clusters.

Cluster Model	Shape	No. of C / H	E_{ads} (eV)	Deviation	E_{gap} (eV)
Standard Square	Square	103 / 28	-1.124	Reference	2.24
Large Hexagonal	Hexagonal	149 / 30	-1.144	1.80%	2.21
Large Square	Square	169 / 36	-1.153	2.60%	2.19

Table S8. The calculated electronic transition of pristine DTPA in water: excitation energy, maximum absorption wavelength, oscillator strength, and transition dipole moment.

Excited State	Energy (eV)	Wavelength (nm)	f	Transition dipole moment (a.u.)
S1	4.929475	251.5	0.000224	0.043012
S2	5.018202	247.1	0.010473	0.291873
S3	5.043458	245.8	0.002744	0.14903
S4	5.120079	242.2	0.001775	0.118954
S5	5.218743	237.6	0.002315	0.134573
S6	5.31544	233.3	0.000745	0.075631
S7	5.371793	230.8	0.000898	0.082583
S8	5.441	227.9	0.001145	0.092682
S9	5.496837	225.6	0.001568	0.107935
S10	5.542205	223.7	0.003138	0.15202
S11	5.613812	220.9	0.001447	0.102567
S12	5.7563	215.4	0.003708	0.162142
S13	5.807482	213.5	0.008259	0.240936
S14	5.827926	212.7	0.002721	0.138058
S15	5.84145	212.2	0.000793	0.074431

Table S9. The calculated electronic transition of pristine DTPA@pris_graphene in water: excitation energy, maximum absorption wavelength, oscillator strength, and transition dipole moment.

Excited State	Energy (eV)	Wavelength (nm)	f	Transition dipole moment (a.u.)
S1	1.616301	767.1	0.048908	1.111346
S2	2.019027	614.1	0.174122	1.876193
S3	2.487802	498.4	0.000141	0.048166
S4	2.619492	473.3	0.05648	0.93812
S5	2.824601	438.9	0.002118	0.174957
S6	2.874088	431.4	0.016045	0.477347
S7	3.120679	397.3	0.04823	0.794242
S8	3.538841	350.4	0.010155	0.342243
S9	3.665296	338.3	0.001528	0.130422
S10	3.907622	317.3	2.87E-05	0.017321
S11	4.012643	309	0.001894	0.138816
S12	4.202994	295	0.000923	0.094657
S13	4.426006	280.1	0.000863	0.089219
S14	4.700222	263.8	0.001778	0.124258
S15	4.966134	249.7	0.000225	0.043012

Table S10. The calculated electronic transition of pristine DTPA@SW_graphene in water: excitation energy, maximum absorption wavelength, oscillator strength, and transition dipole moment.

Excited State	Energy (eV)	Wavelength (nm)	f	Transition dipole moment (a.u.)
S1	0.787866	1573.7	6.27E-05	0.057009
S2	1.045562	1185.8	0.006816	0.515839
S3	1.495965	828.8	0.000774	0.145362
S4	1.641908	755.1	0.000168	0.064653
S5	1.706671	726.5	0.004338	0.322102
S6	1.785043	694.6	0.009962	0.477274
S7	2.18206	568.2	0.003851	0.268403
S8	2.476527	500.6	0.011231	0.430244
S9	2.727646	454.5	0.026757	0.632764
S10	3.093597	400.8	0.029491	0.623779
S11	3.157027	392.7	0.011329	0.382714
S12	3.258904	380.4	0.019707	0.49681
S13	3.380011	366.8	0.019096	0.480219
S14	3.536667	350.6	2.87E-05	0.018166
S15	3.63202	341.4	3.89E-05	0.020976