[Supporting Information]

Tracing the Transition from Covalent to Non-covalent Functionalization of Pyrene through C-, N-, and O- based Ionic and Radical Substrates using Quantum Mechanical Calculations

Anwesh Pandey*, Nandan Kumar*

Advanced Computation and Data Sciences Division, CSIR-North East Institute of Science and Technology, Jorhat-785006, Assam, India

*Corresponding Authors Email: apdapbbau@gmail.com, mr.kumarnandan@gmail.com

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Table S7(C): The variation of electron density (ρ), Laplacian of electron density ($\nabla^2\rho$), total energy density (H($\mathbf{r}$)), and the ratio of kinetic energy density G($\mathbf{r}$), and potential energy density V($\mathbf{r}$), (-[G($\mathbf{r}$)/V($\mathbf{r}$)]) obtained at bond critical points for radical substrates with pyrene.
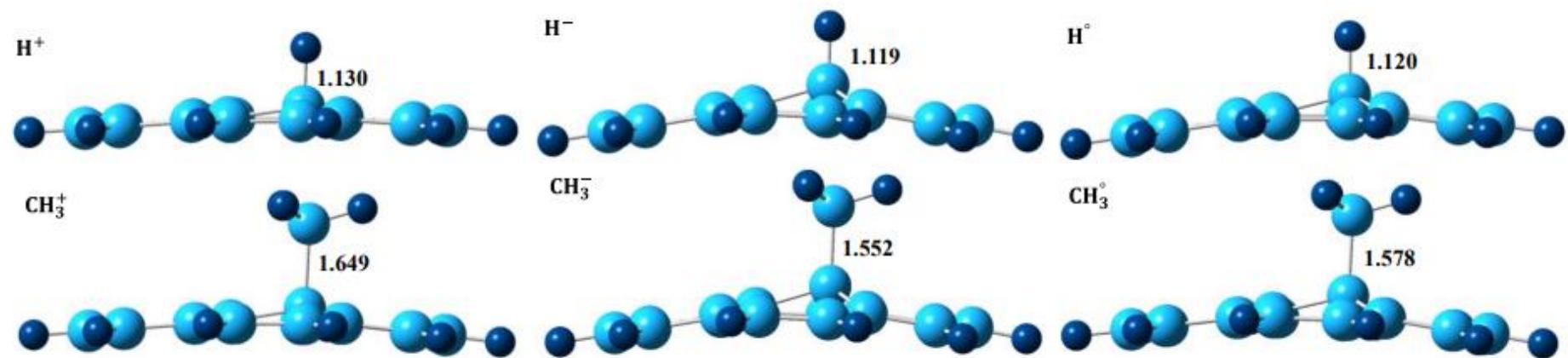
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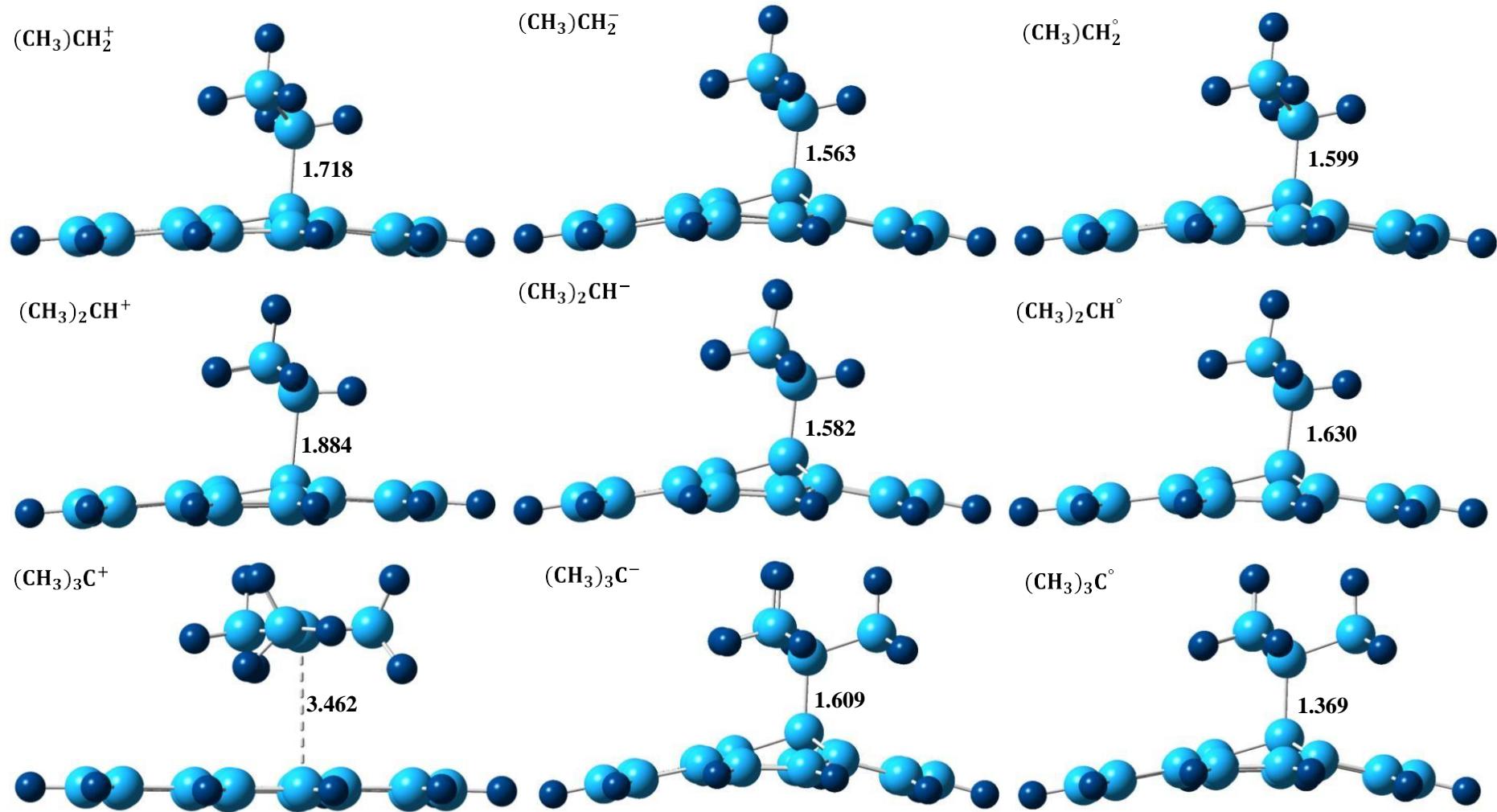
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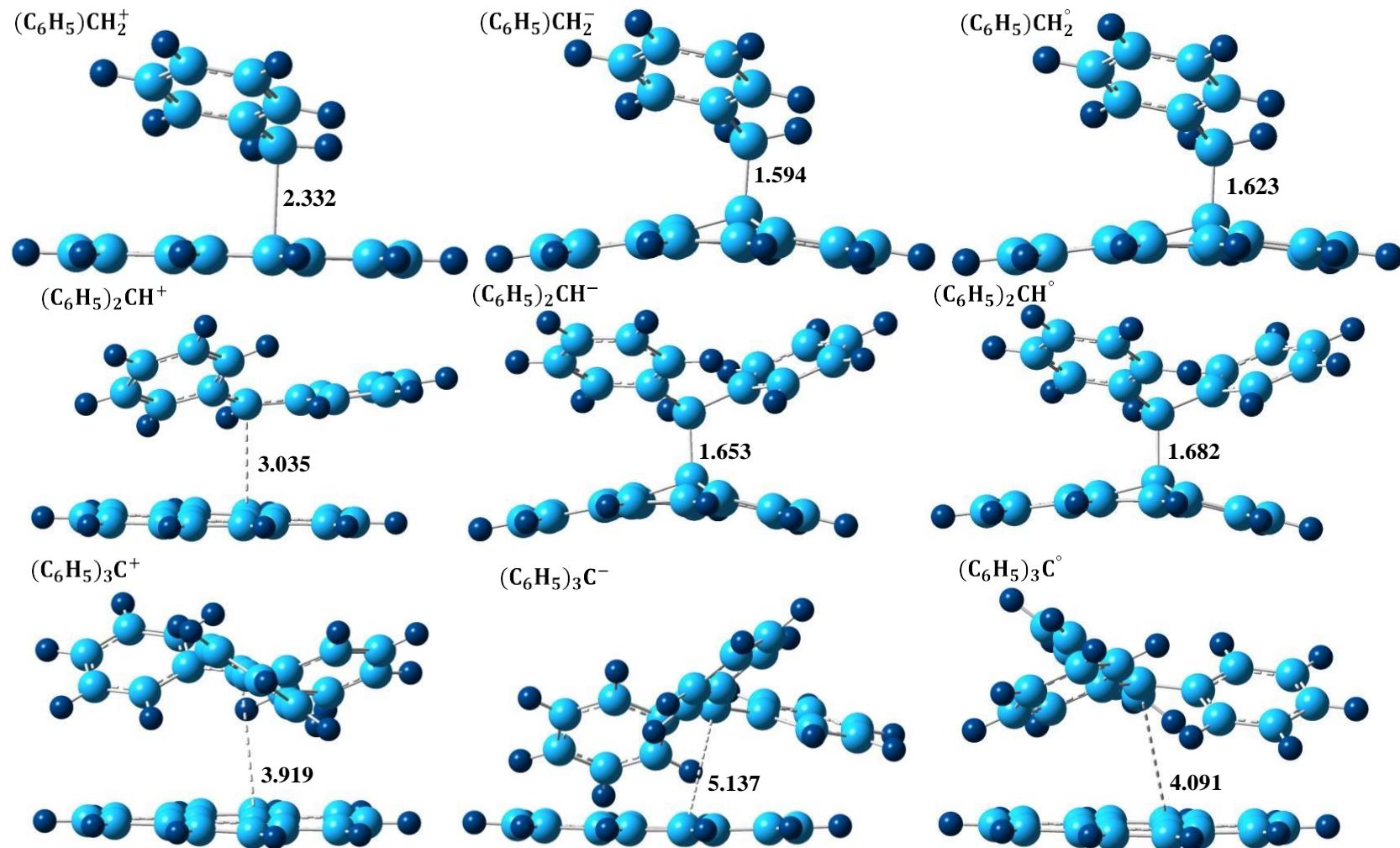
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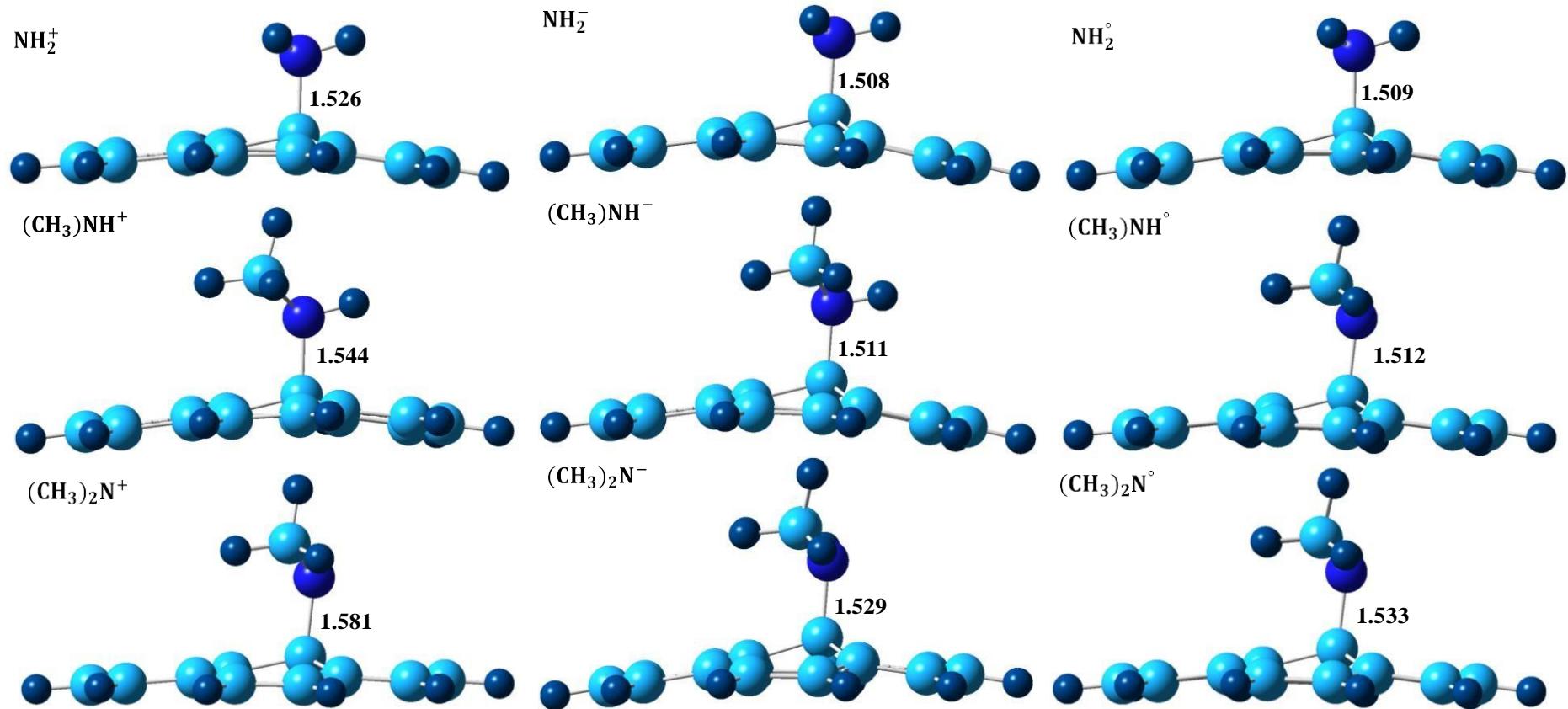
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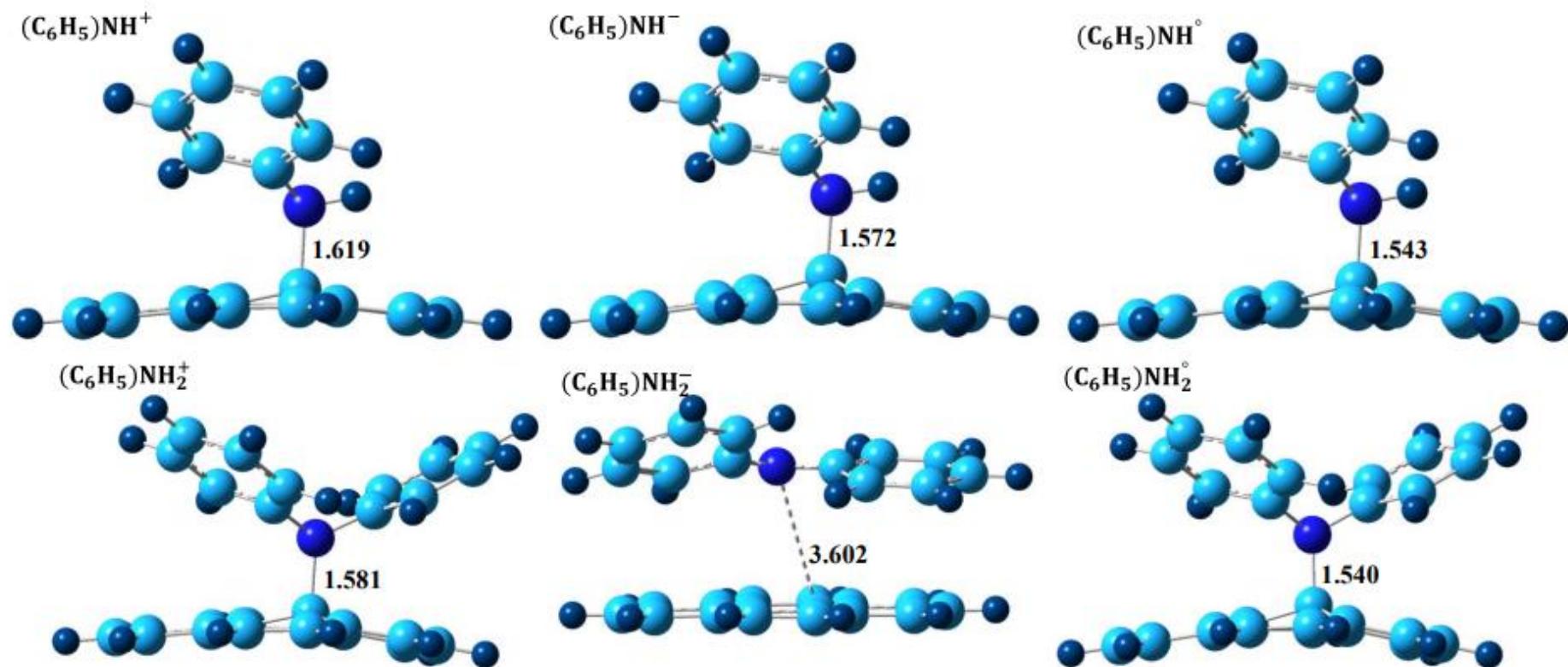
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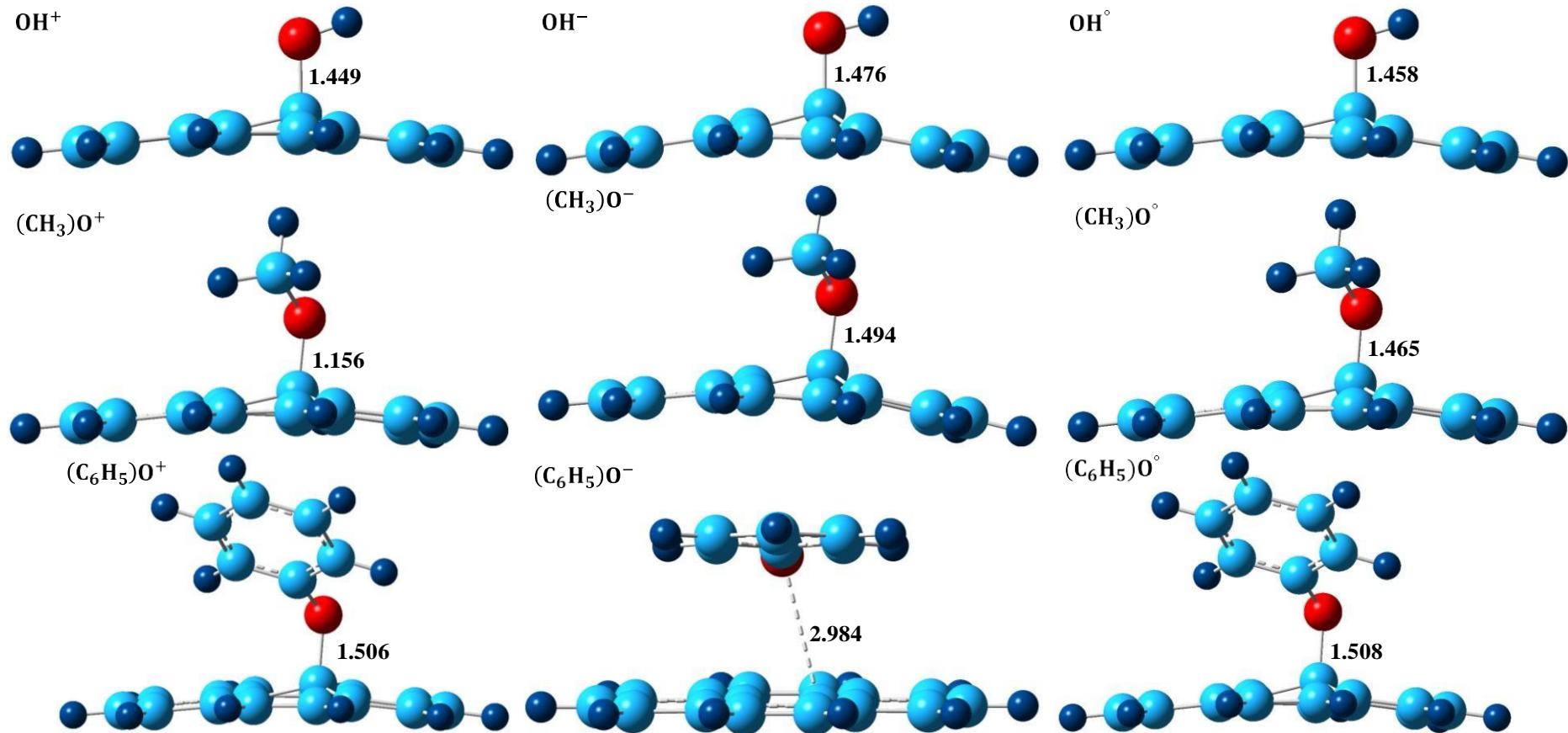
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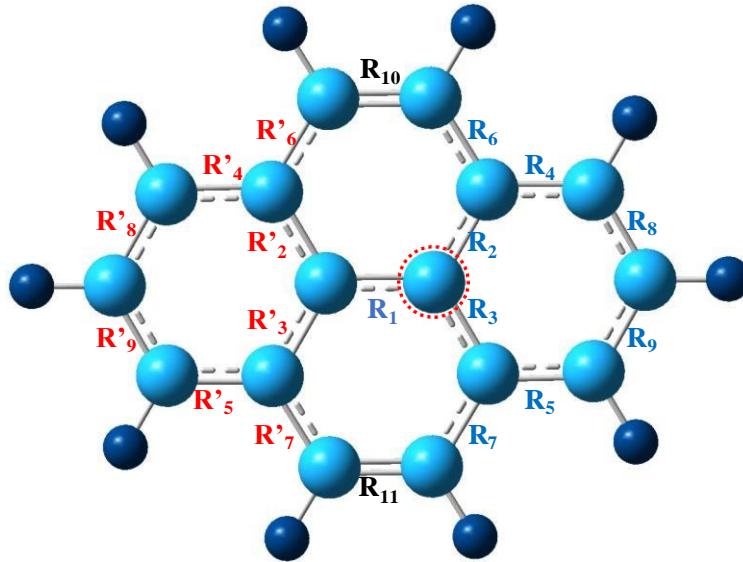
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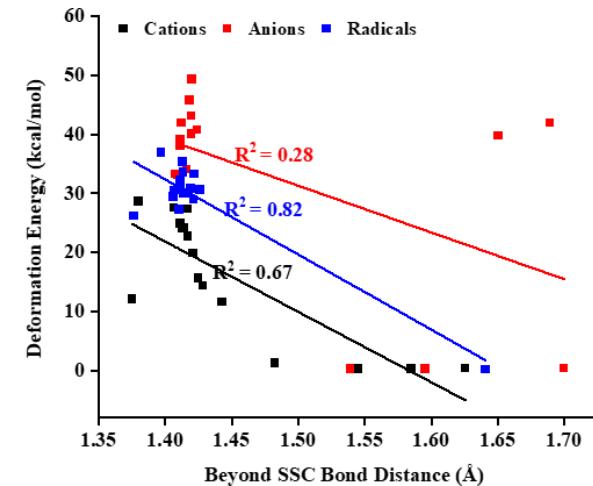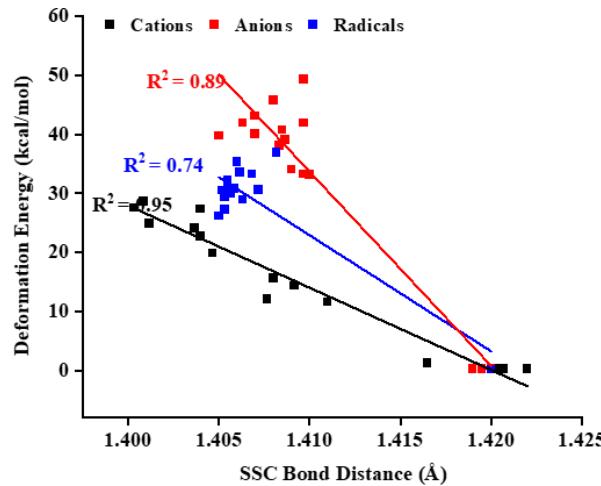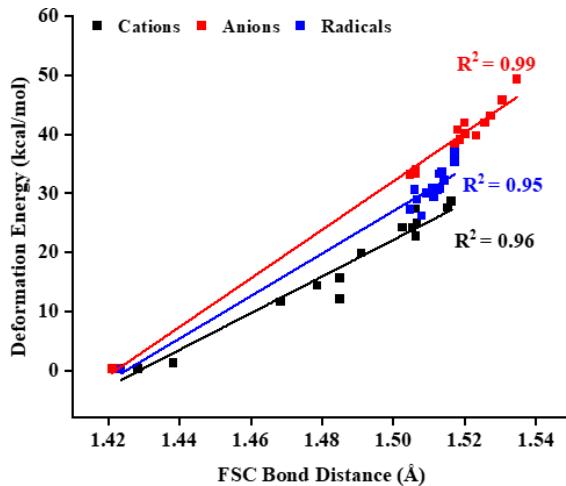
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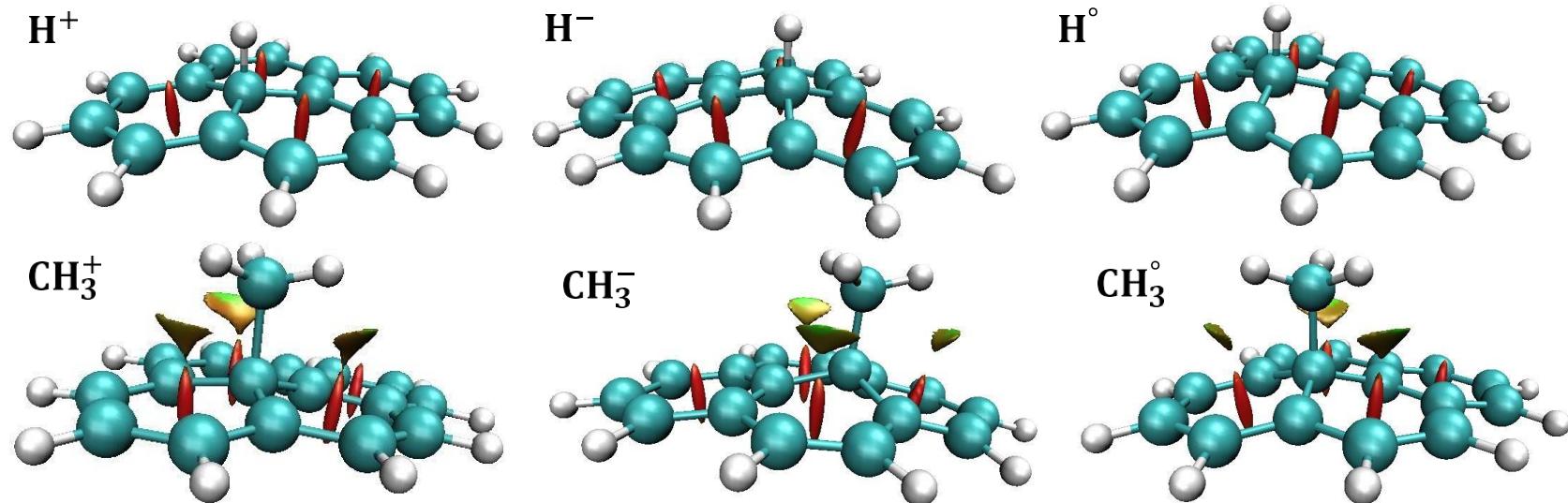
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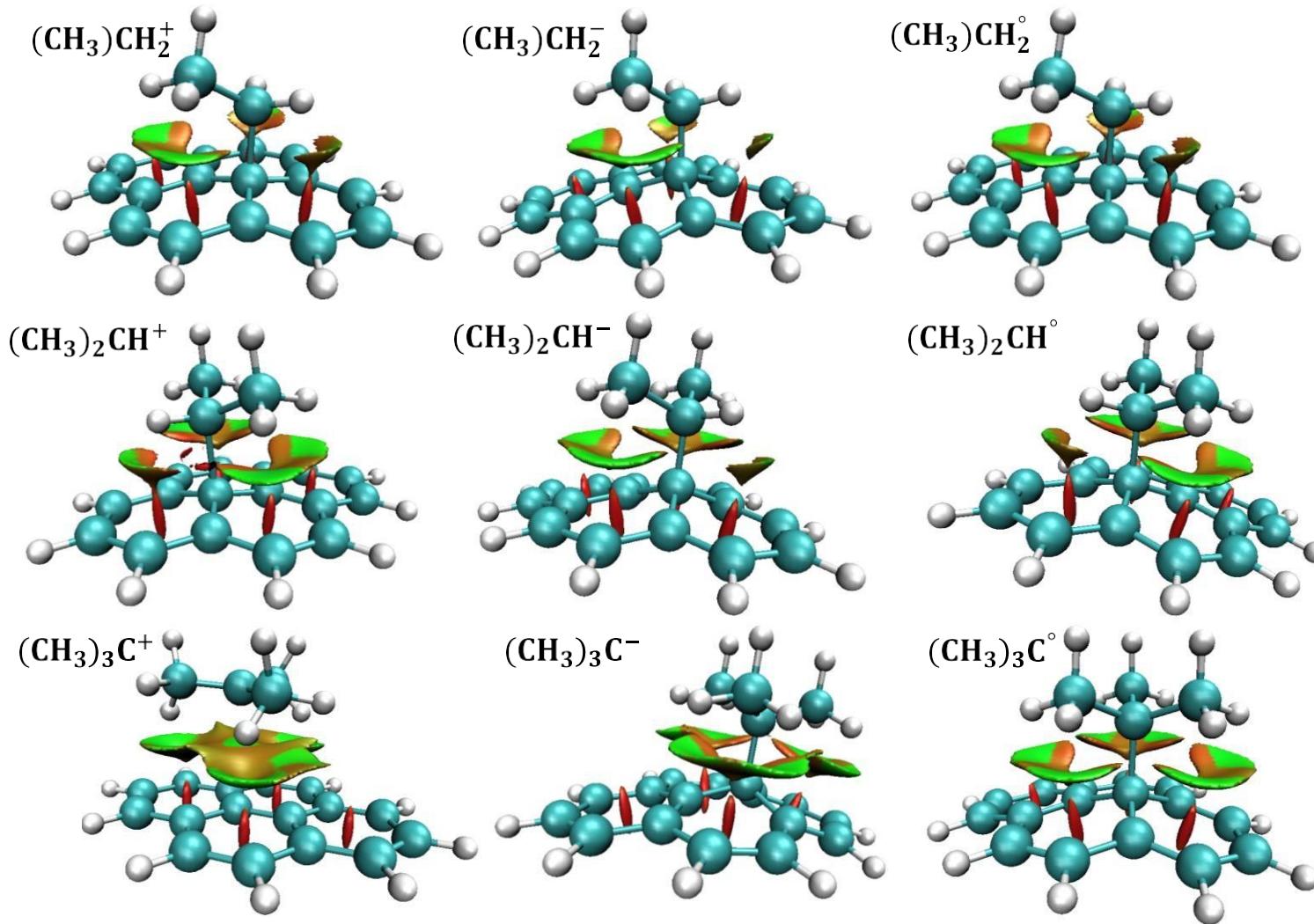
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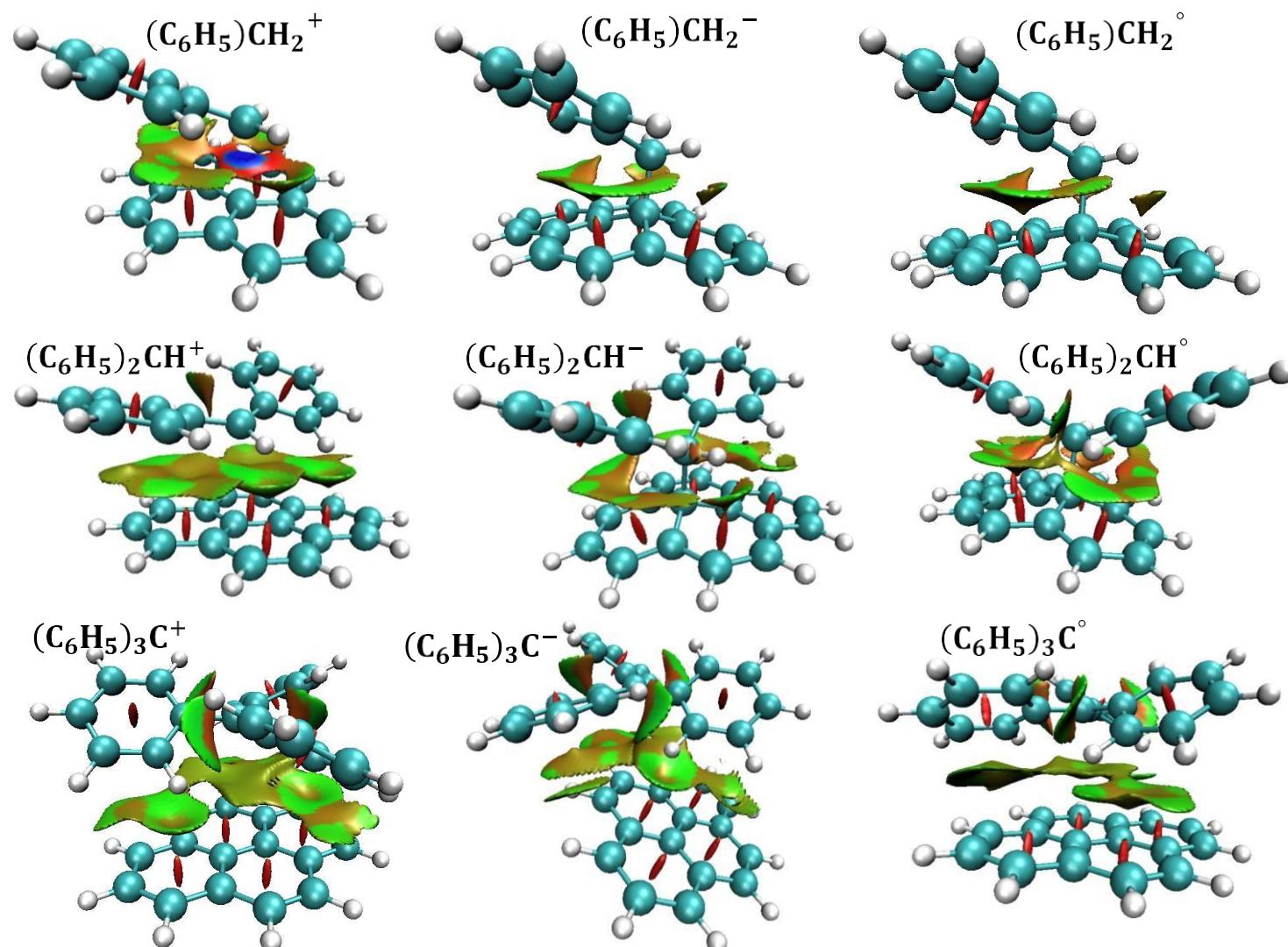
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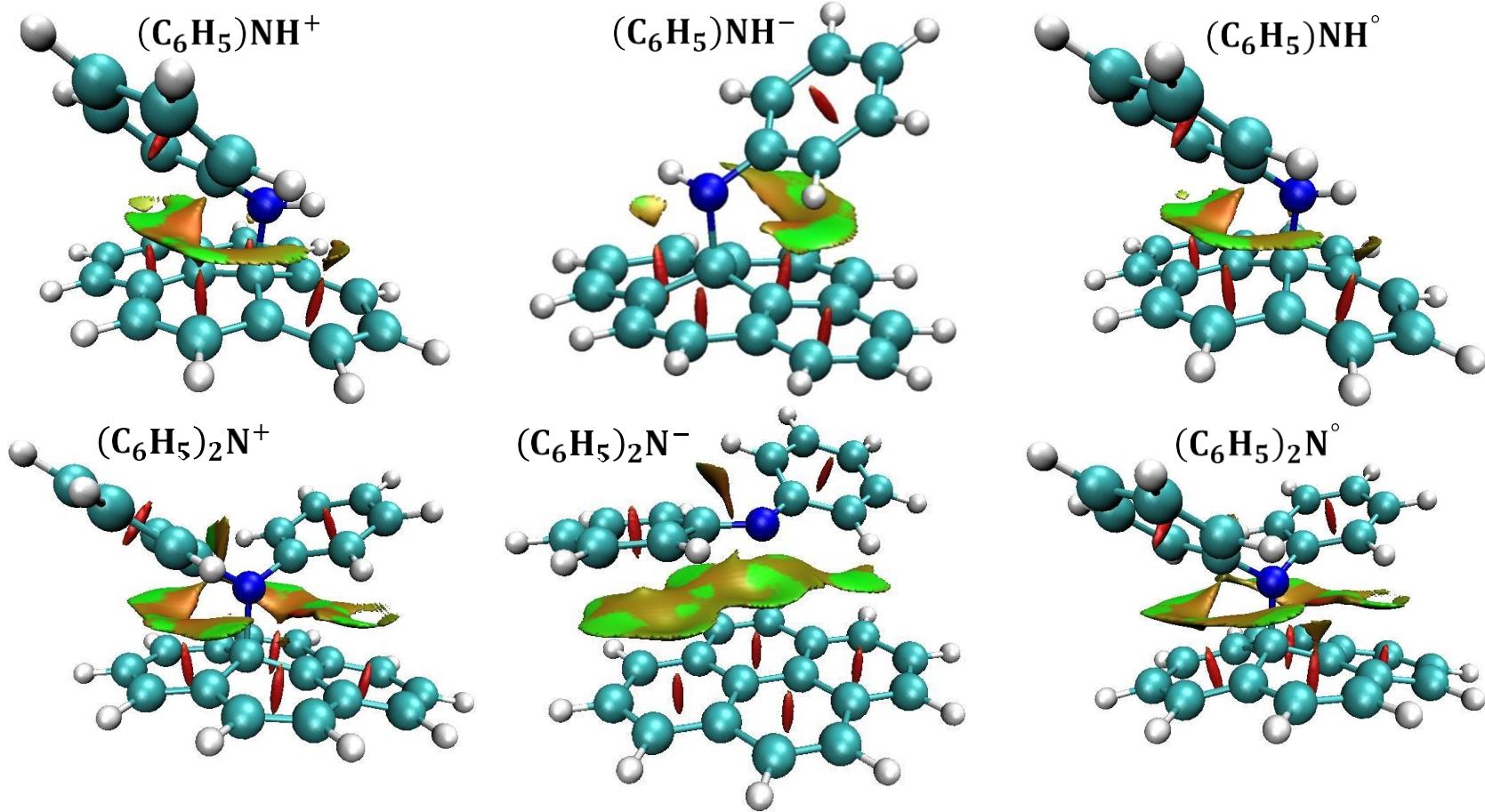
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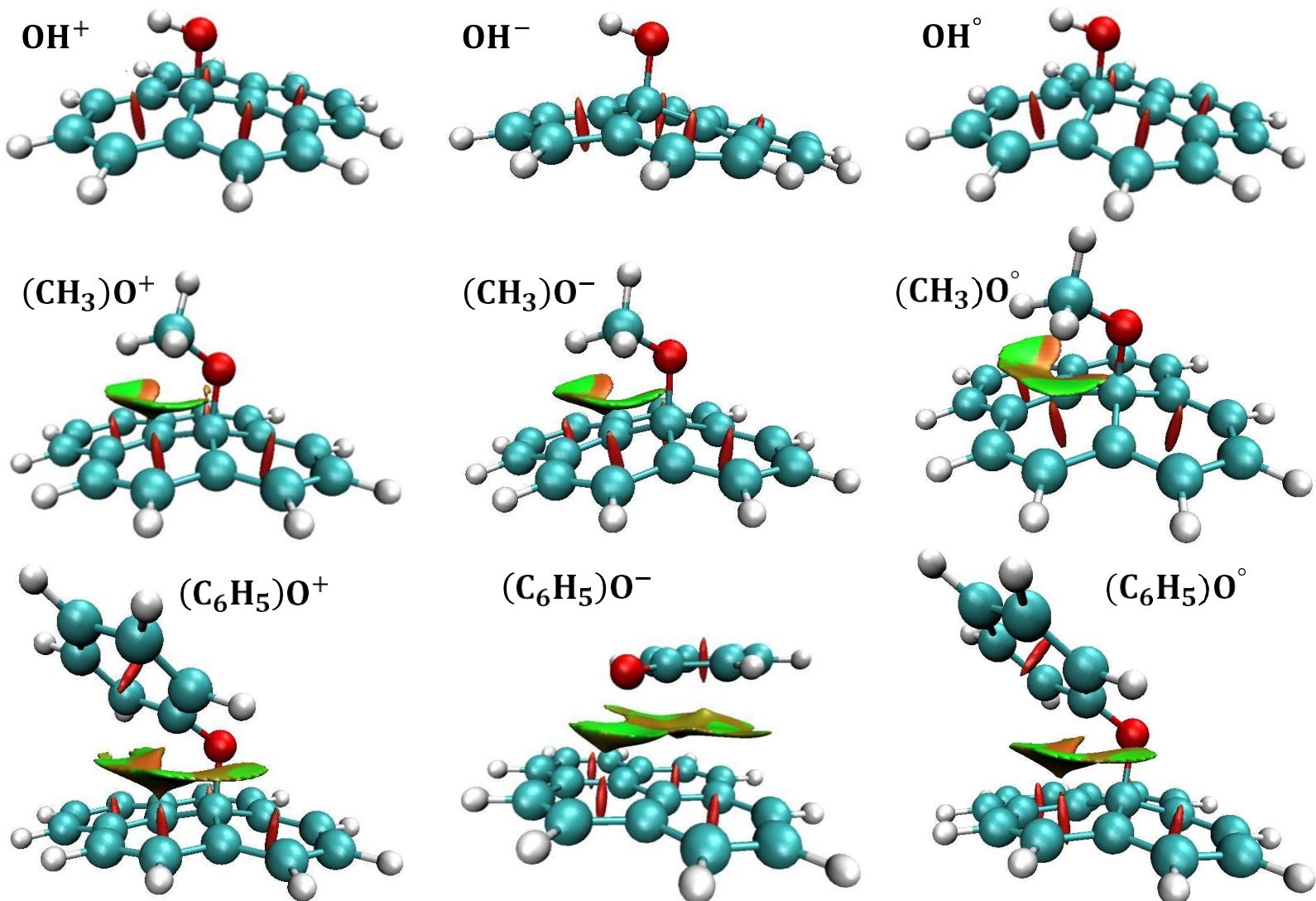
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Table S1: Different methods used for the benchmark study of the interactions between pyrene ($C_{16}H_{10}$) with cationic, anionic, and radical substrates.

Method	Description	Reference
HF	Wave Function Based Method	a
MP2	Post HF Wave Function Based Method	b
BP86	GGA Density Functional Method	c, d
B3LYP	Hybrid-GGA Density Functional Method	e, f
M06	Hybrid Meta-GGA Density Functional Method	g, h
camB3LYP	Range-Separated Hybrid Density Functional Method	i
B3LYP-D3	Hybrid-GGA Density Functional Method with Grimme's Empirical Dispersion Corrections (D3)	j

References:

a. The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part II. Some Results and Discussion by D. R. Hartree, Mathematical Proceedings of the Cambridge Philosophical Society, Volume 24, 111–132, January 1928.
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Table S2(A): Benchmarking of the geometrical parameters of pyrene-H complexes in cationic, anionic, and radical states at different levels of theories. Values are given in Å.

Methods	Cation				Anion				Radical			
	R_0	R_1	R_2	R_3	R_0	R_1	R_2	R_3	R_0	R_1	R_2	R_3
*M06-2X/6-31G**	*1.130*	*1.485*	*1.485*	*1.485*	*1.119*	*1.522*	*1.524*	*1.524*	*1.120*	*1.508*	*1.508*	*1.508*
camB3LYP/6-31G*	1.125	1.486	1.486	1.486	1.120	1.522	1.523	1.523	1.118	1.508	1.509	1.509
camB3LYP/6-311G**	1.126	1.483	1.482	1.482	1.119	1.519	1.521	1.521	1.117	1.506	1.506	1.506
camB3LYP/6-311+G**	1.126	1.483	1.482	1.482	1.121	1.517	1.519	1.519	1.117	1.506	1.506	1.506
B3LYP/6-31G*	1.126	1.491	1.496	1.496	1.123	1.527	1.532	1.532	1.121	1.512	1.517	1.517
B3LYP/6-311G**	1.126	1.488	1.492	1.492	1.121	1.525	1.530	1.530	1.119	1.510	1.514	1.514
B3LYP/6-311+G**	1.126	1.488	1.492	1.492	1.123	1.523	1.528	1.528	1.120	1.510	1.514	1.514
BP86/6-31G*	1.135	1.495	1.502	1.502	1.132	1.532	1.539	1.539	1.132	1.516	1.522	1.522
BP86/6-311G**	1.135	1.491	1.498	1.498	1.130	1.530	1.536	1.536	1.130	1.514	1.520	1.520
BP86/6-311+G**	1.136	1.491	1.498	1.498	1.131	1.528	1.535	1.535	1.131	1.513	1.519	1.519
M06/6-31G*	1.128	1.482	1.485	1.485	1.126	1.517	1.521	1.521	1.123	1.503	1.506	1.506
M06/6-311G**	1.129	1.478	1.481	1.481	1.126	1.514	1.517	1.517	1.123	1.501	1.503	1.503
M06/6-311+G**	1.130	1.478	1.481	1.481	1.127	1.512	1.516	1.516	1.124	1.500	1.503	1.503
B3LYP-D3/6-31G*	1.125	1.490	1.495	1.495	1.122	1.526	1.532	1.532	1.120	1.512	1.516	1.516
B3LYP-D3/6-311G**	1.125	1.487	1.492	1.492	1.120	1.524	1.529	1.529	1.119	1.510	1.514	1.514
B3LYP-D3/6-311+G**	1.126	1.487	1.491	1.491	1.122	1.522	1.528	1.528	1.120	1.509	1.513	1.513
HF/6-31G*	1.112	1.495	1.488	1.488	1.108	1.524	1.521	1.521	1.101	1.513	1.516	1.516
HF/6-311G**	1.113	1.492	1.486	1.486	1.110	1.521	1.519	1.519	1.102	1.511	1.515	1.515
HF/6-311+G**	1.114	1.492	1.485	1.485	1.112	1.520	1.517	1.517	1.103	1.511	1.514	1.514
MP2/6-31G*	1.132	1.478	1.481	1.481	1.122	1.518	1.525	1.525	1.118	1.508	1.507	1.507
MP2/6-311G**	1.136	1.477	1.482	1.482	1.124	1.518	1.525	1.525	1.118	1.509	1.507	1.507
MP2/6-311+G**	1.137	1.478	1.482	1.482	1.128	1.516	1.522	1.522	1.119	1.509	1.507	1.506

Table S2(B): Benchmarking of the geometrical parameters of pyrene-CH_3 complexes in cationic, anionic, and radical states at different levels of theories. Values are given in Å.

Methods	Cation				Anion				Radical			
	R_0	R_1	R_2	R_3	R_0	R_1	R_2	R_3	R_0	R_1	R_2	R_3
M06-2X/6-31G*	*1.649*	*1.487*	*1.484*	*1.484*	*1.552*	*1.525*	*1.526*	*1.526*	*1.552*	*1.525*	*1.526*	*1.526*
camB3LYP/6-31G*	1.636	1.491	1.487	1.487	1.555	1.527	1.527	1.527	1.576	1.514	1.513	1.513
camB3LYP/6-311G**	1.638	1.489	1.485	1.485	1.554	1.525	1.526	1.526	1.575	1.513	1.512	1.512
camB3LYP/6-311+G**	1.638	1.489	1.485	1.485	1.556	1.525	1.525	1.525	1.576	1.513	1.512	1.512
B3LYP/6-31G*	1.652	1.494	1.497	1.497	1.565	1.533	1.536	1.536	1.589	1.518	1.521	1.521
B3LYP/6-311G**	1.654	1.493	1.494	1.494	1.565	1.531	1.535	1.535	1.589	1.517	1.520	1.520
B3LYP/6-311+G**	1.655	1.493	1.494	1.494	1.567	1.531	1.535	1.535	1.590	1.517	1.519	1.519
BP86/6-31G*	1.655	1.498	1.503	1.503	1.569	1.537	1.543	1.543	1.595	1.521	1.526	1.526
BP86/6-311G**	1.655	1.496	1.501	1.501	1.568	1.536	1.541	1.541	1.594	1.520	1.525	1.525
BP86/6-311+G**	1.656	1.496	1.501	1.501	1.570	1.535	1.540	1.540	1.595	1.520	1.524	1.524
M06/6-31G*	1.632	1.485	1.486	1.486	1.548	1.522	1.525	1.525	1.570	1.508	1.511	1.511
M06/6-311G**	1.632	1.483	1.484	1.484	1.547	1.520	1.523	1.523	1.569	1.507	1.509	1.509
M06/6-311+G**	1.633	1.483	1.483	1.483	1.549	1.519	1.522	1.522	1.571	1.507	1.508	1.508
B3LYP-D3/6-31G*	1.653	1.493	1.496	1.496	1.563	1.531	1.535	1.535	1.588	1.516	1.520	1.520
B3LYP-D3/6-311G**	1.655	1.491	1.494	1.494	1.563	1.530	1.534	1.534	1.588	1.515	1.519	1.519
B3LYP-D3/6-311+G**	1.655	1.491	1.493	1.493	1.565	1.529	1.534	1.534	1.589	1.515	1.518	1.518
HF/6-31G*	1.629	1.501	1.491	1.491	1.555	1.530	1.526	1.526	1.567	1.520	1.522	1.522
HF/6-311G**	1.631	1.499	1.489	1.489	1.556	1.529	1.525	1.525	1.567	1.519	1.521	1.521
HF/6-311+G**	1.632	1.499	1.489	1.489	1.558	1.529	1.525	1.525	1.568	1.519	1.521	1.521
MP2/6-31G*	1.655	1.478	1.480	1.480	1.546	1.519	1.526	1.526	1.569	1.510	1.508	1.508
MP2/6-311G**	1.666	1.476	1.479	1.479	1.549	1.520	1.527	1.527	1.573	1.510	1.508	1.508
MP2/6-311+G**	1.661	1.478	1.480	1.480	1.554	1.520	1.526	1.526	1.577	1.510	1.508	1.508

Table S2(C): Benchmarking of the geometrical parameters of pyrene-$(CH_3)_3C$ complexes in cationic, anionic, and radical states at different levels of theories. Values are given in Å.

Methods	Cation				Anion				Radical			
	R_0	R_1	R_2	R_3	R_0	R_1	R_2	R_3	R_0	R_1	R_2	R_3
M06-2X/6-31G*	*3.462*	*1.431*	*1.427*	*1.427*	*1.609*	*1.536*	*1.534*	*1.534*	*1.369*	*1.520*	*1.516*	*1.516*
camB3LYP/6-31G*	3.360	1.429	1.421	1.423	1.619	1.537	1.535	1.535	1.667	1.523	1.520	1.520
camB3LYP/6-311G**	3.403	1.427	1.419	1.420	1.616	1.536	1.534	1.534	1.667	1.522	1.518	1.518
camB3LYP/6-311+G**	3.427	1.427	1.419	1.420	1.617	1.536	1.534	1.534	1.669	1.522	1.517	1.517
B3LYP/6-31G*	3.465	1.428	1.429	1.432	1.639	1.543	1.544	1.544	1.706	1.525	1.524	1.524
B3LYP/6-311G**	3.491	1.426	1.427	1.430	1.637	1.542	1.543	1.543	1.708	1.523	1.522	1.522
B3LYP/6-311+G**	3.512	1.427	1.427	1.430	1.638	1.542	1.542	1.542	1.711	1.523	1.522	1.522
BP86/6-31G*	3.471	1.431	1.437	1.441	1.642	1.546	1.549	1.549	1.721	1.525	1.527	1.527
BP86/6-311G**	3.450	1.430	1.435	1.438	1.639	1.545	1.548	1.548	1.721	1.523	1.525	1.525
BP86/6-311+G**	3.465	1.430	1.435	1.438	1.640	1.545	1.547	1.547	1.724	1.523	1.525	1.525
M06/6-31G*	3.133	1.425	1.425	1.428	1.611	1.533	1.533	1.533	1.666	1.517	1.516	1.516
M06/6-311G**	3.141	1.422	1.423	1.425	1.610	1.530	1531	1531	1.665	1.514	1.514	1.514
M06/6-311+G**	3.176	1.422	1.422	1.424	1.611	1.530	1.531	1.531	1.668	1.514	1.513	1.513
B3LYP-D3/6-31G*	3.253	1.428	1.429	1.433	1.634	1.540	1.543	1.543	1.701	1.522	1.523	1.523
B3LYP-D3/6-311G**	3.262	1.426	1.427	1.430	1.632	1.539	1.542	1.542	1.703	1.521	1.521	1.521
B3LYP-D3/6-311+G**	3.275	1.426	1.427	1.430	1.633	1.539	1.541	1.541	1.705	1.520	1.521	1.521
HF/6-31G*	3.623	1.435	1.414	1.414	1.619	1.544	1.536	1.536	1.645	1.533	1.532	1.532
HF/6-311G**	3.698	1.434	1.413	1.413	1.619	1.543	1.536	1.536	1.647	1.531	1.531	1.531
HF/6-311+G**	3.730	1.434	1.413	1.413	1.621	1.543	1.536	1.536	1.648	1.531	1.531	1.531
MP2/6-31G*	2.840	1.427	1.437	1.437	1.597	1.529	1.534	1.534	1.647	1.519	1.515	1.515
MP2/6-311G**	2.734	1.429	1.441	1.441	1.594	1.528	1.534	1.534	1.646	1.518	1.514	1.514
MP2/6-311+G**	2.814	1.428	1.440	1.440	1.599	1.528	1.534	1.534	1.653	1.518	1.514	1.514

Table S3(A): The geometrical parameters for cationic substrates interacting pyrene obtained at M06-2X/6-31G* level of theory.

System	R0	R1	R2	R2'	R3	R3'	R4	R4'	R5	R5'	R6	R6'	R7	R7'	R8	R8'	R9	R9'	R10	R11
Pristine	-	1.428	1.421	1.421	1.421	1.421	1.399	1.399	1.399	1.399	1.440	1.440	1.440	1.440	1.391	1.391	1.391	1.391	1.354	1.354
H^+	1.130	1.485	1.485	1.407	1.485	1.407	1.386	1.400	1.386	1.400	1.430	1.449	1.430	1.449	1.399	1.391	1.399	1.391	1.360	1.360
CH_3^+	1.649	1.487	1.484	1.407	1.484	1.407	1.386	1.400	1.386	1.400	1.431	1.407	1.431	1.449	1.399	1.391	1.399	1.400	1.390	1.390
$(CH_3)CH_2^+$	1.718	1.480	1.481	1.409	1.475	1.408	1.386	1.400	1.390	1.401	1.432	1.449	1.430	1.448	1.400	1.391	1.397	1.391	1.359	1.360
$(CH_3)_2CH^+$	1.884	1.468	1.468	1.411	1.469	1.411	1.390	1.400	1.390	1.400	1.432	1.447	1.432	1.447	1.398	1.391	1.398	1.391	1.358	1.358
$(CH_3)_3C^+$	3.462	1.431	1.427	1.421	1.427	1.421	1.399	1.399	1.400	1.400	1.442	1.443	1.441	1.444	1.394	1.392	1.395	1.392	1.357	1.357
$(C_6H_5)CH_2^+$	2.332	1.440	1.438	1.418	1.437	1.415	1.394	1.400	1.399	1.400	1.439	1.444	1.434	1.444	1.397	1.393	1.392	1.391	1.357	1.359
$(C_6H_5)_2CH^+$	3.035	1.429	1.420	1.424	1.422	1.423	1.400	1.398	1.401	1.399	1.442	1.441	1.442	1.441	1.392	1.393	1.393	1.392	1.355	1.357
$(C_6H_5)_3C^+$	3.919	1.428	1.421	1.421	1.422	1.421	1.399	1.400	1.400	1.400	1.441	1.441	1.441	1.441	1.392	1.393	1.392	1.393	1.356	1.354
NH_2^+	1.526	1.504	1.507	1.401	1.505	1.401	1.382	1.400	1.383	1.401	1.424	1.452	1.431	1.455	1.403	1.391	1.402	1.390	1.361	1.360
$(CH_3)NH^+$	1.544	1.500	1.509	1.400	1.499	1.403	1.374	1.400	1.393	1.401	1.429	1.456	1.423	1.450	1.412	1.392	1.392	1.390	1.357	1.363
$(CH_3)_2N^+$	1.581	1.499	1.510	1.407	1.510	1.407	1.380	1.401	1.380	1.401	1.425	1.450	1.425	1.450	1.402	1.390	1.402	1.390	1.361	1.361
$(C_6H_5)NH^+$	1.619	1.489	1.497	1.402	1.487	1.402	1.374	1.400	1.397	1.401	1.431	1.455	1.422	1.451	1.413	1.393	1.388	1.390	1.356	1.363
$(C_6H_5)_2N^+$	1.581	1.499	1.510	1.407	1.510	1.407	1.380	1.401	1.380	1.401	1.425	1.450	1.425	1.450	1.402	1.390	1.402	1.390	1.361	1.361
OH^+	1.449	1.510	1.518	1.398	1.518	1.398	1.380	1.400	1.380	1.400	1.423	1.455	1.423	1.454	1.405	1.391	1.405	1.391	1.362	1.362
$(CH_3)O^+$	1.156	1.510	1.523	1.401	1.516	1.399	1.379	1.399	1.376	1.402	1.422	1.455	1.428	1.458	1.401	1.392	1.407	1.390	1.362	1.360
$(C_6H_5)O^+$	1.506	1.501	1.512	1.401	1.507	1.400	1.374	1.400	1.384	1.401	1.427	1.456	1.421	1.454	1.408	1.393	1.398	1.390	1.358	1.364

Table S3(B): The geometrical parameters for anionic substrates interacting pyrene obtained at M06-2X/6-31G* level of theory.

System	R0	R1	R2	R2'	R3	R3'	R4	R4'	R5	R5'	R6	R6'	R7	R7'	R8	R8'	R9	R9'	R10	R11
Pristine	-	1.428	1.421	1.421	1.421	1.421	1.399	1.399	1.399	1.399	1.440	1.440	1.440	1.440	1.391	1.391	1.391	1.391	1.354	1.354
H$^-$	1.119	1.522	1.524	1.409	1.524	1.409	1.383	4.404	1.383	1.404	1.423	1.453	1.423	1.453	1.405	1.391	1.405	1.391	1.365	1.365
CH$_3$$^-$	1.552	1.525	1.526	1.411	1.526	1.411	1.384	1.403	1.384	4.404	1.424	1.452	1.424	1.452	1.404	1.391	1.404	1.391	1.364	1.364
(CH$_3$)CH$_2$$^-$	1.563	1.527	1.528	1.412	1.527	1.412	1.384	1.43	1.385	1.404	1.424	1.451	1.425	1.451	1.403	1.391	1.404	1.391	1.364	1.363
(CH$_3$)$_2$CH$^-$	1.582	1.530	1.531	1.414	1.531	1.414	1.386	1.404	1.386	1.404	1.424	1.451	1.424	1.451	1.403	1.390	1.403	1.390	1.362	1.362
(CH$_3$)$_3$C$^-$	1.609	1.536	1.534	1.415	1.534	1.415	1.387	1.404	1.387	1.404	1.427	1.449	1.427	1.450	1.401	1.390	1.401	1.390	1.361	1.361
(C$_6$H$_5$)CH$_2$$^-$	1.594	1.519	1.522	1.412	1.520	1.411	1.387	1.404	1.382	1.403	1.422	1.451	1.428	1.451	1.401	1.391	1.407	1.391	1.365	1.360
(C$_6$H$_5$)$_2$CH$^-$	1.653	1.518	1.520	1.412	1.516	1.412	1.388	1.404	1.386	1.402	1.423	1.449	1.430	1.448	1.397	1.391	1.403	1.391	1.366	1.360
(C$_6$H$_5$)$_3$C$^-$	4.743	1.427	1.420	1.422	1.421	1.422	1.398	1.399	1.399	1.401	1.441	1.441	1.438	1.438	1.391	1.392	1.391	1.391	1.355	1.356
NH$_2$$^-$	1.508	1.517	1.516	1.412	1.519	1.412	1.383	1.402	1.389	1.404	1.428	1.450	1.426	1.450	1.406	1.392	1.400	1.390	1.360	1.364
(CH$_3$)NH$^-$	1.511	1.518	1.518	1.413	1.520	1.413	1.384	1.402	1.389	1.405	1.428	1.450	1.425	1.449	1.405	1.392	1.400	1.390	1.360	1.363
(CH$_3$)$_2$N$^-$	1.529	1.522	1.519	1.416	1.519	1.416	1.387	1.404	1.387	1.404	1.426	1.449	1.426	1.449	1.399	1.390	1.399	1.390	1.362	1.362
(C$_6$H$_5$)NH$^-$	1.572	1.504	1.507	1.413	1.508	1.413	1.386	1.403	1.388	1.403	1.426	1.448	1.428	1.447	1.402	1.392	1.402	1.390	1.361	1.360
(C$_6$H$_5$)$_2$N$^-$	3.602	1.428	1.419	1.420	1.420	1.419	1.397	1.397	1.401	1.400	1.440	1.441	1.440	1.440	1.393	1.391	1.390	1.390	1.353	1.355
OH$^-$	1.476	1.505	1.507	1.412	1.507	1.412	1.388	1.403	1.388	1.403	1.429	1.449	1.429	1.449	1.402	1.391	1.402	1.391	1.360	1.360
(CH$_3$)O$^-$	1.494	1.507	1.503	1.415	1.504	1.415	1.385	1.402	1.391	1.405	1.428	1.448	1.426	1.447	1.402	1.392	1.396	1.390	1.360	1.363
(C$_6$H$_5$)O$^-$	2.984	1.426	1.418	1.418	1.419	1.419	1.400	1.400	1.397	1.397	1.441	1.441	1.439	1.439	1.389	1.389	1.393	1.393	1.352	1.352

Table S3(C): The geometrical parameters for radical substrates interacting with pyrene obtained at M06-2X/6-31G* level of theory.

System	R0	R1	R2	R2'	R3	R3'	R4	R4'	R5	R5'	R6	R6'	R7	R7'	R8	R8'	R9	R9'	R10	R11
Pristine	-	1.428	1.421	1.421	1.421	1.421	1.399	1.399	1.399	1.399	1.440	1.440	1.440	1.440	1.391	1.391	1.391	1.391	1.354	1.354
H˚	1.120	1.508	1.508	1.404	1.508	1.404	1.380	1.401	1.380	1.401	1.431	1.455	1.431	1.455	1.405	1.391	1.405	1.391	1.358	1.358
CH_3	1.578	1.511	1.511	1.405	1.511	1.405	1.381	1.401	1.381	1.401	1.431	1.454	1.431	1.454	1.404	1.390	1.405	1.390	1.358	1.358
$(CH_3)CH_2$	1.599	1.511	1.513	1.406	1.509	1.406	1.380	1.401	1.383	1.401	1.430	1.454	1.430	1.454	1.405	1.390	1.403	1.390	1.358	1.358
$(CH_3)_2CH˚$	1.630	1.511	1.514	1.408	1.514	1.408	1.383	1.401	1.382	1.401	1.430	1.454	1.430	1.454	1.404	1.390	1.404	1.390	1.357	1.357
$(CH_3)_3C˚$	1.369	1.520	1.516	1.409	1.516	1.409	1.383	1.401	1.382	1.401	1.433	1.453	1.433	1.453	1.402	1.389	1.402	1.389	1.355	1.355
$(C_6H_5)CH_2$	1.623	1.506	1.509	1.407	1.505	1.406	1.381	1.401	1.384	1.401	1.431	1.454	1.429	1.453	1.405	1.391	1.403	1.390	1.358	1.358
$(C_6H_5)_2CH˚$	1.682	1.509	1.507	1.408	1.502	1.406	1.380	1.401	1.383	1.400	1.433	1.454	1.433	1.452	1.402	1.391	1.402	1.390	1.358	1.356
$(C_6H_5)_3C˚$	4.091	1.430	1.420	1.420	1.421	1.422	1.399	1.398	1.398	1.399	1.441	1.441	1.440	1.441	1.390	1.390	1.390	1.391	1.361	1.358
NH_2	1.509	1.512	1.513	1.404	1.514	1.404	1.379	1.400	1.383	1.402	1.431	1.454	1.432	1.456	1.407	1.391	1.403	1.390	1.356	1.358
$(CH_3)NH˚$	1.512	1.513	1.516	1.405	1.514	1.404	1.377	1.400	1.386	1.402	1.432	1.455	1.429	1.454	1.410	1.391	1.400	1.389	1.355	1.359
$(CH_3)_2N˚$	1.533	1.516	1.518	1.408	1.518	1.408	1.380	1.401	1.380	1.401	1.430	1.454	1.430	1.454	1.403	1.390	1.403	1.390	1.357	1.357
$(C_6H_5)NH˚$	1.543	1.506	1.512	1.405	1.510	1.404	1.377	1.400	1.387	1.401	1.432	1.454	1.428	1.453	1.410	1.392	1.399	1.390	1.355	1.358
$(C_6H_5)_2N˚$	1.540	1.514	1.514	1.405	1.513	1.404	1.375	1.400	1.386	1.401	1.435	1.455	1.432	1.453	1.408	1.391	1.399	1.389	1.355	1.357
OH˚	1.458	1.508	1.513	1.403	1.513	1.403	1.381	1.400	1.381	1.400	1.432	1.455	1.432	1.455	1.405	1.390	1.405	1.390	1.356	1.356
$(CH_3)O˚$	1.465	1.511	1.514	1.406	1.512	1.405	1.377	1.399	1.381	1.402	1.431	1.455	1.431	1.455	1.405	1.392	1.403	1.389	1.356	1.358
$(C_6H_5)O˚$	1.508	1.503	1.507	1.406	1.504	1.404	1.376	1.400	1.385	1.401	1.432	1.454	1.429	1.453	1.407	1.392	1.399	1.390	1.356	1.358

Table S4(A): Benchmarking of the interaction energies (IE; kcal/mol) of pyrene-H complexes in cationic, anionic, and radical states at different levels of theories. The value obtained at M06-2X/6-311G**//M06-2X/6-31G* level of theory is considered as a reference (energy zero) to calculate the absolute relative energy (RE; kcal/mol).

Methods	Cation	RE	Anion	RE	Radical	RE
*M06-2X/6-311G**//M06-2X/6-31G**	*-197.03*	*0.00*	*-74.44*	*0.00*	*-37.65*	*0.00*
M06-2X/6-311G**//camB3LYP/6-31G*	-197.81	0.78	-73.63	0.81	-37.73	0.08
M06-2X/6-311G**//camB3LYP/6-311G**	-196.85	0.18	-73.17	1.27	-37.40	0.25
M06-2X/6-311G**//camB3LYP/6-311+G**	-196.83	0.20	-72.28	2.16	-37.13	0.52
M06-2X/6-311G**//B3LYP/6-31G*	-199.11	2.08	-74.39	0.05	-38.29	0.64
M06-2X/6-311G**//B3LYP/6-311G**	-198.20	1.17	-73.95	0.49	-37.96	0.31
M06-2X/6-311G**//B3LYP/6-311+G**	-198.19	1.16	-73.08	1.36	-37.68	0.03
M06-2X/6-311G**//BP86/6-31G*	-199.21	2.18	-75.74	1.30	-38.46	0.81
M06-2X/6-311G**//BP86/6-311G**	-198.18	1.15	-75.39	0.95	-38.10	0.45
M06-2X/6-311G**//BP86/6-311+G**	-198.19	1.16	-74.64	0.20	-37.84	0.19
M06-2X/6-311G**//M06/6-31G*	-197.44	0.41	-73.06	1.38	-36.65	1.00
M06-2X/6-311G**//M06/6-311G**	-196.51	0.52	-72.49	1.95	-36.37	1.28
M06-2X/6-311G**//M06/6-311+G**	-196.42	0.61	-71.67	2.77	-36.03	1.62
M06-2X/6-311G**//B3LYP-D3/6-31G*	-199.01	1.98	-74.30	0.14	-38.17	0.52
M06-2X/6-311G**//B3LYP-D3/6-311G**	-198.09	1.06	-73.86	0.58	-37.84	0.19
M06-2X/6-311G**//B3LYP-D3/6-311+G**	-198.08	1.05	-72.99	1.45	-37.57	0.08
M06-2X/6-311G**//HF/6-31G*	-200.71	3.68	-73.11	1.33	-39.67	2.02
M06-2X/6-311G**//HF/6-311G**	-200.04	3.01	-72.74	1.70	-39.49	1.84
M06-2X/6-311G**//HF/6-311+G**	-199.95	2.92	-71.79	2.65	-39.24	1.59
M06-2X/6-311G**//MP2/6-31G*	-196.18	0.85	-76.30	1.86	-39.12	1.47
M06-2X/6-311G**//MP2/6-311G**	-194.55	2.48	-76.62	2.18	-39.30	1.65
M06-2X/6-311G**//MP2/6-311+G**	-194.94	2.09	-75.27	0.83	-39.23	1.58

Table S4(B): Benchmarking of the interaction energies (IE, kcal/mol) of pyrene-CH₃ complexes in cationic, anionic, and radical states at different levels of theories. The value obtained at M06-2X/6-311G**//M06-2X/6-31G* level of theory is considered as a reference (energy zero) to calculate the absolute relative energy (RE; kcal/mol).

Methods	Cation	RE	Anion	RE	Radical	RE
*M06-2X/6-311G**//M06-2X/6-31G**	-126.43	*0.00*	-82.07	*0.00*	-37.69	*0.00*
M06-2X/6-311G**//camB3LYP/6-31G*	-130.07	3.64	-82.23	0.16	-38.97	1.28
M06-2X/6-311G**//camB3LYP/6-311G**	-129.72	3.29	-82.03	0.04	-39.02	1.33
M06-2X/6-311G**//camB3LYP/6-311+G**	-129.6	3.17	-81.78	0.29	-38.91	1.22
M06-2X/6-311G**//B3LYP/6-31G*	-130.47	4.04	-83.32	1.25	-39.67	1.98
M06-2X/6-311G**//B3LYP/6-311G**	-130.05	3.62	-83.12	1.05	-39.54	1.85
M06-2X/6-311G**//B3LYP/6-311+G**	-129.91	3.48	-82.83	0.76	-39.44	1.75
M06-2X/6-311G**//BP86/6-31G*	-130.03	3.60	-84.30	2.23	-39.52	1.83
M06-2X/6-311G**//BP86/6-311G**	-129.66	3.23	-84.04	1.97	-39.31	1.62
M06-2X/6-311G**//BP86/6-311+G**	-129.46	3.03	-83.82	1.75	-39.22	1.53
M06-2X/6-311G**//M06/6-31G*	-129.43	3.00	-81.34	0.73	-37.85	0.16
M06-2X/6-311G**//M06/6-311G**	-129.00	2.57	-80.96	1.11	-37.69	0.00
M06-2X/6-311G**//M06/6-311+G**	-128.77	2.34	-80.64	1.43	-37.55	0.14
M06-2X/6-311G**//B3LYP-D3/6-31G*	-129.66	3.23	-82.72	0.65	-38.99	1.30
M06-2X/6-311G**//B3LYP-D3/6-311G**	-129.23	2.80	-82.52	0.45	-38.85	1.16
M06-2X/6-311G**//B3LYP-D3/6-311+G**	-129.09	2.66	-82.22	0.15	-38.75	1.06
M06-2X/6-311G**//HF/6-31G*	-134.64	8.21	-82.52	0.45	-42.09	4.40
M06-2X/6-311G**//HF/6-311G**	-134.14	7.71	-82.42	0.35	-42.00	4.31
M06-2X/6-311G**//HF/6-311+G**	-134.03	7.60	-82.13	0.06	-41.95	4.26
M06-2X/6-311G**//MP2/6-31G*	-123.57	2.86	-83.32	1.25	-38.58	0.89
M06-2X/6-311G**//MP2/6-311G**	-121.01	5.42	-82.79	0.72	-37.78	0.09
M06-2X/6-311G**//MP2/6-311+G**	-122.7	3.73	-82.49	0.42	-37.87	0.18

Table S4(C): Benchmarking of the interaction energies (IE, kcal/mol) of pyrene-$(CH_3)_3C$ complexes in cationic, anionic, and radical states at different levels of theories. The value obtained at M06-2X/6-311G**//M06-2X/6-31G* level of theory is considered as a reference (energy zero) to calculate the absolute relative energy (RE; kcal/mol).

Methods	Cation	RE	Anion	RE	Radical	RE
*M06-2X/6-311G**//M06-2X/6-31G*	*-24.96*	*0.00*	*-85.11*	*0.00*	*-36.52*	*0.00*
M06-2X/6-311G**//camB3LYP/6-31G*	-23.49	1.47	-85.69	0.58	-38.77	2.25
M06-2X/6-311G**//camB3LYP/6-311G**	-23.09	1.87	-85.64	0.53	-38.38	1.86
M06-2X/6-311G**//camB3LYP/6-311+G**	-22.90	2.06	-85.46	0.35	-38.25	1.73
M06-2X/6-311G**//B3LYP/6-31G*	-22.70	2.26	-86.41	1.30	-37.45	0.93
M06-2X/6-311G**//B3LYP/6-311G**	-22.32	2.64	-86.37	1.26	-36.91	0.39
M06-2X/6-311G**//B3LYP/6-311+G**	-22.10	2.86	-86.15	1.04	-36.70	0.18
M06-2X/6-311G**//BP86/6-31G*	-22.76	2.20	-86.44	1.33	-35.66	0.86
M06-2X/6-311G**//BP86/6-311G**	-22.87	2.09	-86.29	1.18	-34.99	1.53
M06-2X/6-311G**//BP86/6-311+G**	-22.71	2.25	-86.07	0.96	-34.72	1.80
M06-2X/6-311G**//M06/6-31G*	-24.46	0.50	-84.54	0.57	-36.88	0.36
M06-2X/6-311G**//M06/6-311G**	-24.36	0.60	-84.18	0.93	-36.52	0.00
M06-2X/6-311G**//M06/6-311+G**	-24.17	0.79	-83.82	1.29	-36.28	0.24
M06-2X/6-311G**//B3LYP-D3/6-31G*	-24.27	0.69	-85.77	0.66	-36.78	0.26
M06-2X/6-311G**//B3LYP-D3/6-311G**	-24.08	0.88	-85.72	0.61	-36.24	0.28
M06-2X/6-311G**//B3LYP-D3/6-311+G**	-24.05	0.91	-85.48	0.37	-36.03	0.49
M06-2X/6-311G**//HF/6-31G*	-20.41	4.55	-87.80	2.69	-43.91	7.39
M06-2X/6-311G**//HF/6-311G**	-19.69	5.27	-87.79	2.68	-43.72	7.20
M06-2X/6-311G**//HF/6-311+G**	-19.26	5.70	-87.64	2.53	-43.69	7.17
M06-2X/6-311G**//MP2/6-31G*	-25.99	1.03	-85.85	0.74	-38.22	1.70
M06-2X/6-311G**//MP2/6-311G**	-25.63	0.67	-84.64	0.47	-37.22	0.70
M06-2X/6-311G**//MP2/6-311+G**	-25.86	0.90	-84.24	0.87	-37.17	0.65

Table S5(A). Contribution of each energy component into the interaction energy (IE; kcal/mol) of cationic substrates-pyrene complexes obtained using LMOEDA scheme at M06-2X/6-311G** level of theory.

Systems	Electrostatic	Exchange	Repulsion	Polarization	Dispersion	IE
H^+	35.790	0.000	0.000	-232.950	0.050	-197.120
CH_3^+	-45.330	-68.910	217.240	-200.990	-28.470	-126.480
$(CH_3)CH_2^+$	-52.710	-75.420	231.380	-164.520	-33.390	-94.650
$(CH_3)_2CH^+$	-46.600	-62.210	189.690	-110.800	-37.560	-67.480
$(CH_3)_3C^+$	-18.250	-13.730	47.720	-12.550	-28.240	-25.050
$(C_6H_5)CH_2^+$	-27.530	-31.200	96.280	-31.730	-33.190	-27.370
$(C_6H_5)_2CH^+$	-15.580	-15.830	54.530	-7.560	-34.500	-18.940
$(C_6H_5)_3C^+$	-12.450	-12.740	47.090	-4.150	-32.740	-14.990
NH_2^+	-101.410	-128.560	419.860	-320.420	-29.890	-160.420
$(CH_3)NH^+$	-121.220	-148.460	472.270	-281.490	-35.180	-114.070
$(CH_3)_2N^+$	-125.790	-155.120	483.910	-248.170	-42.070	-87.230
$(C_6H_5)NH^+$	-112.610	-145.080	439.970	-197.030	-41.390	-56.140
$(C_6H_5)_2N^+$	-120.830	-158.370	477.320	-195.810	-54.270	-51.950
OH^+	-76.790	-116.230	400.250	-418.360	-29.860	-241.000
$(CH_3)O^+$	-108.910	-149.300	492.000	-363.560	-33.910	-163.670
$(C_6H_5)O^+$	-123.790	-161.910	505.390	-251.470	-40.320	-72.110

Table S5(B). Contribution of each energy component into the interaction energy (IE; kcal/mol) of anionic substrates-pyrene complexes obtained using LMOEDA scheme at M06-2X/6-311G** level of theory.

Systems	Electrostatic	Exchange	Repulsion	Polarization	Dispersion	IE
H^-	-208.570	-272.840	724.780	-287.610	-30.090	-74.320
CH_3^-	-292.220	-320.910	904.180	-334.550	-38.190	-81.690
$(CH_3)CH_2^-$	-295.310	-321.290	909.360	-336.440	-43.100	-86.780
$(CH_3)_2CH^-$	-283.020	-310.400	879.020	-324.340	-48.760	-87.500
$(CH_3)_3C^-$	-261.590	-293.530	828.330	-303.840	-54.330	-84.970
$(C_6H_5)CH_2^-$	-217.130	-253.600	715.440	-256.130	-44.880	-56.300
$(C_6H_5)_2CH^-$	-175.230	-219.020	615.880	-209.770	-52.790	-40.920
$(C_6H_5)_3C^-$	-9.520	-17.010	52.550	-6.770	-30.870	-11.620
NH_2^-	-265.400	-299.430	843.730	-312.150	-36.040	-69.280
$(CH_3)NH^-$	-255.080	-287.240	816.060	-303.480	-41.370	-71.100
$(CH_3)_2N^-$	-229.340	-267.100	760.340	-280.970	-48.010	-65.070
$(C_6H_5)NH^-$	-177.400	-221.980	629.230	-218.510	-41.690	-30.350
$(C_6H_5)_2N^-$	-5.060	-17.610	52.380	-8.020	-28.780	-7.080
OH^-	-229.770	-268.770	756.310	-280.920	-32.080	-55.230
$(CH_3)O^-$	-201.820	-241.020	682.700	-250.840	-37.600	-48.580
$(C_6H_5)O^-$	-2.000	-18.220	51.730	-11.310	-24.140	-3.940

Table S5(C). Contribution of each energy component into the interaction energy (IE; kcal/mol) of cationic radical-pyrene complexes obtained using LMOEDA scheme at M06-2X/6-311G** level of theory.

Systems	Electrostatic	Exchange	Repulsion	Polarization	Dispersion	IE
H°	-	-	-	-	-	-350.330
CH$_3$°	-133.930	-162.680	480.620	-187.210	-34.450	-37.650
(CH$_3$)CH$_2$°	-135.430	-164.530	483.540	-180.590	-39.830	-36.840
(CH$_3$)$_2$CH°	-131.790	-162.340	473.640	-170.240	-45.760	-36.480
(CH$_3$)$_3$C°	-125.140	-157.690	456.200	-158.500	-51.350	-36.480
(C$_6$H$_5$)CH$_2$°	-128.300	-161.700	472.100	-167.780	-45.260	-30.930
(C$_6$H$_5$)$_2$CH°	-116.430	-153.820	444.360	-146.120	-54.370	-26.380
(C$_6$H$_5$)$_3$C°	-7.520	-13.070	45.760	-2.780	-30.820	-8.440
NH$_2$°	-156.020	-190.760	572.440	-217.890	-35.080	-27.310
(CH$_3$)NH°	-167.730	-201.700	605.260	-219.020	-40.530	-23.730
(CH$_3$)$_2$N°	-169.910	-205.840	613.880	-210.590	-47.280	-19.740
(C$_6$H$_5$)NH°	-154.120	-192.460	573.410	-198.870	-44.460	-16.500
(C$_6$H$_5$)$_2$N°	-166.750	-204.610	617.460	-206.900	-56.050	-16.850
OH°	-127.480	-169.350	516.810	-218.810	-33.290	-32.120
(CH$_3$)O°	-136.760	-178.970	544.980	-213.850	-38.720	-23.320
(C$_6$H$_5$)O°	-131.600	-174.590	523.730	-186.510	-41.390	-10.350

Table S6(A). Percentage contribution of each energy component into the interaction energy of cationic substrates-pyrene complexes obtained using LMOEDA scheme at M06-2X/6-311G** level of theory.

Systems	Electrostatic	Exchange	Polarization	Dispersion
H^+	-18.16	0.00	118.18	-0.03
CH_3^+	13.19	20.05	58.48	8.28
$(CH_3)CH_2^+$	16.17	23.13	50.46	10.24
$(CH_3)_2CH^+$	18.12	24.19	43.08	14.61
$(CH_3)_3C^+$	25.08	18.87	17.25	38.81
$(C_6H_5)CH_2^+$	22.26	25.23	25.66	26.84
$(C_6H_5)_2CH^+$	21.21	21.55	10.29	46.96
$(C_6H_5)_3C^+$	20.05	20.52	6.68	52.74
NH_2^+	17.48	22.15	55.22	5.15
$(CH_3)NH^+$	20.67	25.32	48.01	6.00
$(CH_3)_2N^+$	22.02	27.16	43.45	7.37
$(C_6H_5)NH^+$	22.70	29.24	39.71	8.34
$(C_6H_5)_2N^+$	22.83	29.92	37.00	10.25
OH^+	11.98	18.13	65.24	4.66
$(CH_3)O^+$	16.61	22.77	55.45	5.17
$(C_6H_5)O^+$	21.44	28.04	43.55	6.98

Table S6(B). Percentage contribution of each energy component into the interaction energy of anionic substrates-pyrene complexes obtained using LMOEDA scheme at M06-2X/6-311G** level of theory.

Systems	Electrostatic	Exchange	Polarization	Dispersion
H^-	26.10	34.14	35.99	3.77
CH_3^-	29.64	32.55	33.93	3.87
$(CH_3)CH_2^-$	29.65	32.25	33.77	4.33
$(CH_3)_2CH^-$	29.28	32.12	33.56	5.04
$(CH_3)_3C^-$	28.64	32.14	33.27	5.95
$(C_6H_5)CH_2^-$	28.14	32.86	33.19	5.82
$(C_6H_5)_2CH^-$	26.68	33.35	31.94	8.04
$(C_6H_5)_3C^-$	14.84	26.51	10.55	48.11
NH_2^-	29.07	32.80	34.19	3.95
$(CH_3)NH^-$	28.75	32.38	34.21	4.66
$(CH_3)_2N^-$	27.78	32.36	34.04	5.82
$(C_6H_5)NH^-$	26.90	33.65	33.13	6.32
$(C_6H_5)_2N^-$	8.51	29.61	13.49	48.39
OH^-	28.31	33.12	34.62	3.95
$(CH_3)O^-$	27.60	32.96	34.30	5.14
$(C_6H_5)O^-$	3.59	32.73	20.32	43.36

Table S6(C). Percentage contribution of each energy component into the interaction energy of cationic substrates-pyrene complexes obtained using LMOEDA scheme at M06-2X/6-311G** level of theory.

Systems	Electrostatic	Exchange	Polarization	Dispersion
H°	-	-	-	-
CH$_3$°	25.84	31.39	36.12	6.65
(CH$_3$)CH$_2$°	26.03	31.62	34.70	7.65
(CH$_3$)$_2$CH°	25.83	31.82	33.37	8.97
(CH$_3$)$_3$C°	25.40	32.01	32.17	10.42
(C$_6$H$_5$)CH$_2$°	25.50	32.14	33.35	9.00
(C$_6$H$_5$)$_2$CH°	24.73	32.68	31.04	11.55
(C$_6$H$_5$)$_3$C°	13.88	24.12	5.13	56.87
NH$_2$°	26.01	31.81	36.33	5.85
(CH$_3$)NH°	26.67	32.07	34.82	6.44
(CH$_3$)$_2$N°	26.82	32.49	33.24	7.46
(C$_6$H$_5$)NH°	26.13	32.63	33.71	7.54
(C$_6$H$_5$)$_2$N°	26.29	32.26	32.62	8.84
OH°	23.22	30.85	39.86	6.06
(CH$_3$)O°	24.06	31.49	37.63	6.81
(C$_6$H$_5$)O°	24.64	32.69	34.92	7.75

Table S7(A): The variation of electron density (ρ), Laplacian of electron density ($\nabla^2\rho$), total energy density (H(**r**)), and the ratio of kinetic energy density G(**r**), and potential energy density V(**r**), (-[G(**r**)/V(**r**)]) obtained at bond critical points for cationic substrates with pyrene.

System	ρ	$\nabla^2\rho$	H(r)	(-[G(r)/V(r)])
H^+	0.23836	-0.70453	-0.21889	0.16343
CH_3^+	0.17185	-0.23997	-0.10953	0.31141
$(CH_3)CH_2^+$	0.14761	-0.15500	-0.08277	0.34719
$(CH_3)_2CH^+$	0.02921	0.02090	-0.00737	0.63083
$(CH_3)_3C^+$	0.01050	0.03085	0.00133	1.26408
$(C_6H_5)CH_2^+$	0.01912	0.03610	-0.00101	0.90820
$(C_6H_5)_2CH^+$	0.00885	0.02707	0.00118	1.26881
$(C_6H_5)_3C^+$	0.00829	0.02737	0.00125	1.28904
NH_2^+	0.22744	-0.42137	-0.19288	0.31216
$(CH_3)NH^+$	0.11411	-0.16514	-0.08679	0.34397
$(CH_3)_2N^+$	0.07423	-0.07267	-0.04835	0.38433
$(C_6H_5)NH^+$	0.09614	-0.08058	-0.06016	0.39945
$(C_6H_5)_2N^+$	0.06668	-0.04320	-0.03902	0.41968
OH^+	0.24376	-0.50914	-0.28911	0.35887
$(CH_3)O^+$	0.24060	-0.49276	-0.27343	0.35462
$(C_6H_5)O^+$	0.21252	-0.33722	-0.20419	0.36992

Table S7(B): The variation of electron density (ρ), Laplacian of electron density ($\nabla^2\rho$), total energy density (H($\mathbf{r}$)), and the ratio of kinetic energy density G($\mathbf{r}$), and potential energy density V($\mathbf{r}$), (-[G($\mathbf{r}$)/V($\mathbf{r}$)]) obtained at bond critical points for anionic substrates with pyrene.

System	ρ	$\nabla^2\rho$	H(r)	(-[G(r)/V(r)])
H$^-$	0.25984	-0.81513	-0.24641	0.14747
CH$_3^-$	0.23164	-0.48750	-0.17743	0.23846
(CH$_3$)CH$_2^-$	0.22809	-0.46717	-0.17104	0.24080
(CH$_3$)$_2$CH$^-$	0.22063	-0.43137	-0.15934	0.24425
(CH$_3$)$_3$C$^-$	0.07720	-0.10440	-0.04713	0.30853
(C$_6$H$_5$)CH$_2^-$	0.21092	-0.38417	-0.14861	0.26131
(C$_6$H$_5$)$_2$CH$^-$	0.05388	-0.04692	-0.02839	0.36978
(C$_6$H$_5$)$_3$C$^-$	0.00744	0.02340	0.00098	1.25298
NH$_2^-$	0.24072	-0.54063	-0.23454	0.29762
(CH$_3$)NH$^-$	0.23901	-0.52545	-0.23060	0.30088
(CH$_3$)$_2$N$^-$	0.22908	-0.46986	-0.21112	0.30729
(C$_6$H$_5$)NH$^-$	0.10747	-0.15210	-0.08496	0.35585
(C$_6$H$_5$)$_2$N$^-$	0.00750	0.02230	0.00088	1.23124
OH$^-$	0.22776	-0.41982	-0.26103	0.37419
(CH$_3$)O$^-$	0.21746	-0.36548	-0.23431	0.37890
(C$_6$H$_5$)O$^-$	0.00926	0.02865	0.00103	1.20288

Table S7(C): The variation of electron density (ρ), Laplacian of electron density ($\nabla^2\rho$), total energy density (H(**r**)), and the ratio of kinetic energy density G(**r**), and potential energy density V(**r**), (-[G(**r**)/V(**r**)]) obtained at bond critical points for radical substrates with pyrene.

System	ρ	$\nabla^2\rho$	H(r)	(-[G(r)/V(r)])
H$^\circ$	0.25433	-0.78691	-0.23932	0.15108
CH$_3$$^\circ$	0.21272	-0.40034	-0.15395	0.25919
(CH$_3$)CH$_2$$^\circ$	0.20452	-0.36193	-0.14221	0.26674
(CH$_3$)$_2$CH$^\circ$	0.07190	-0.07701	-0.04090	0.34608
(CH$_3$)$_3$C$^\circ$	0.04476	-0.02285	-0.02064	0.41968
(C$_6$H$_5$)CH$_2$$^\circ$	0.19315	-0.31008	-0.12771	0.28213
(C$_6$H$_5$)$_2$CH$^\circ$	0.06332	-0.05614	-0.03289	0.36435
(C$_6$H$_5$)$_3$C$^\circ$	0.00745	0.02263	0.00099	1.26895
NH$_2$$^\circ$	0.23903	-0.50802	-0.22198	0.29965
(CH$_3$)NH$^\circ$	0.23709	-0.48911	-0.21629	0.30297
(CH$_3$)$_2$N$^\circ$	0.22709	-0.43455	-0.19677	0.30935
(C$_6$H$_5$)NH$^\circ$	0.11458	-0.17981	-0.09261	0.33976
(C$_6$H$_5$)$_2$N$^\circ$	0.07802	-0.11392	-0.06166	0.34985
OH$^\circ$	0.23805	-0.47118	-0.28191	0.36795
(CH$_3$)O$^\circ$	0.23378	-0.44906	-0.26837	0.36776
(C$_6$H$_5$)O$^\circ$	0.20874	-0.32340	-0.20873	0.37991