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UNEXPECTED PHOTOLUMINESCENCE ENHANCEMENT UPON EPOXIDATION OF CORONENE: A DFT/MRCI STUDY

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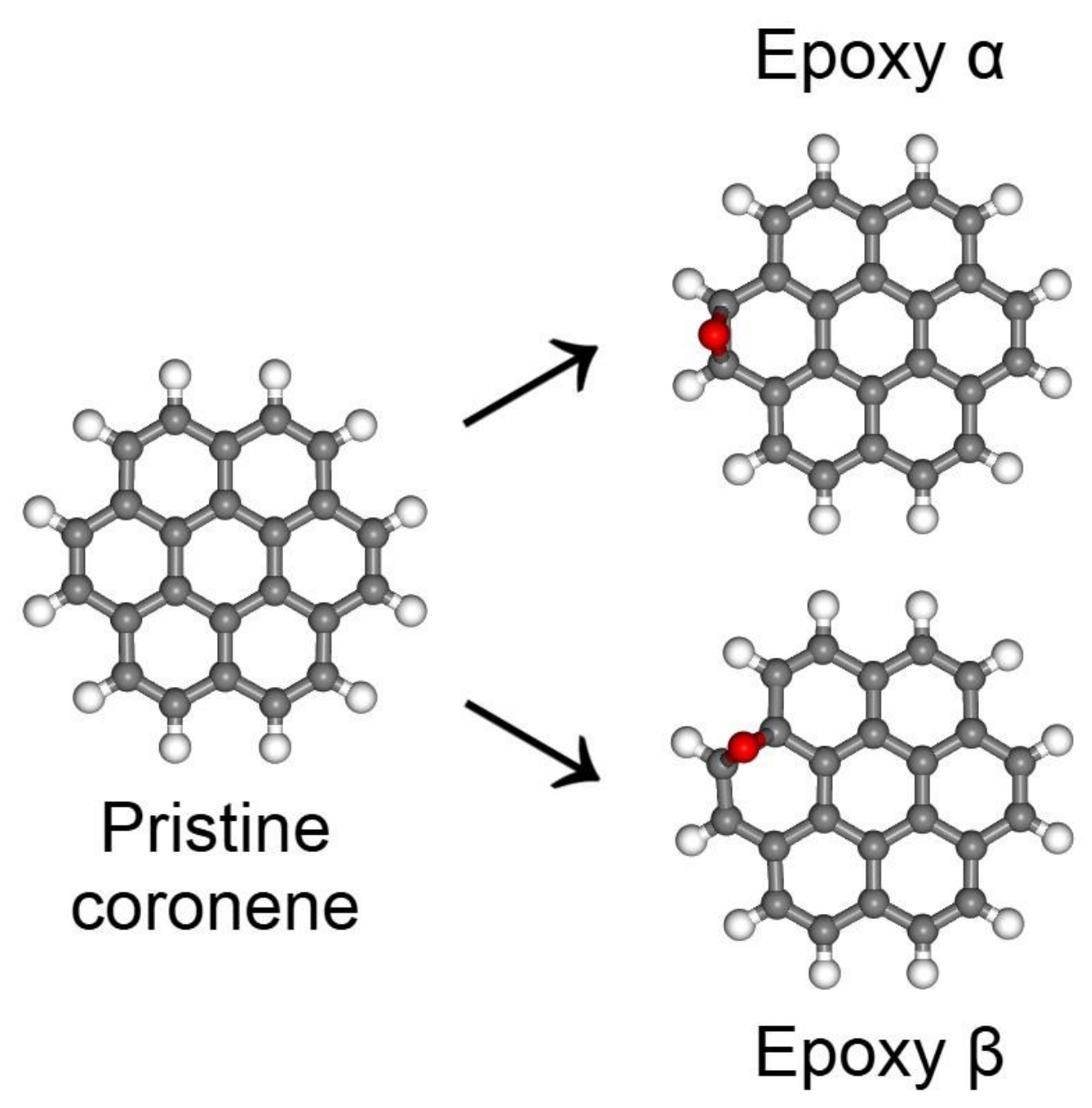
Functionalization of Graphene Quantum Dots

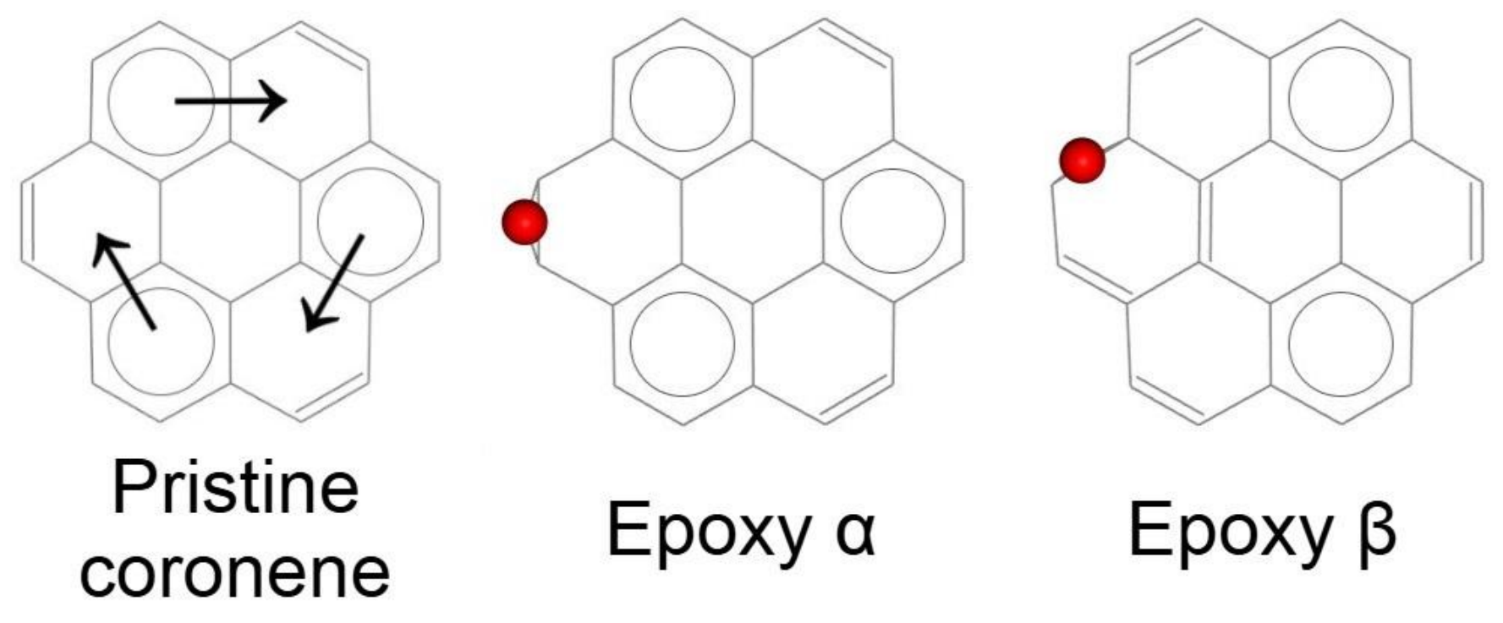
Controlled functionalization of graphene quantum dots (GQDs) represents an effective strategy for tailoring their optical and electronic properties. In particular, epoxidation, which alters the hybridization of carbon atoms from sp² to sp³, can substantially modify the final characteristics of carbon nanostructures. Specifically, epoxidation modulates the band gap width, thereby inducing a bathochromic shift in both absorption and emission bands. Furthermore, epoxidation can enhance the optical response of symmetric GQDs. Meanwhile, investigating coronene as a model GQD revealed an unexpected increase in the $S_0 \leftrightarrow S_1$ transition dipole moment at one of the epoxidation positions.



Structure	Singlet excited state	Absorption edge (nm)	Oscillator strength	Fluorescence (nm)	Oscillator strength
Pristine coronene	S1	404	0.000	431	0.000
	S2	344	0.000	—	—
	S3	294	1.371	—	—
Epoxy α	S1	390	0.002	414	0.002
	S2	373	0.352	—	—
	S3	305	0.004	—	—
Epoxy β	S1	446	0.310	574	0.231
	S2	434	0.021	—	—
	S3	334	0.003	—	—

Disruption of π-Electron Delocalization

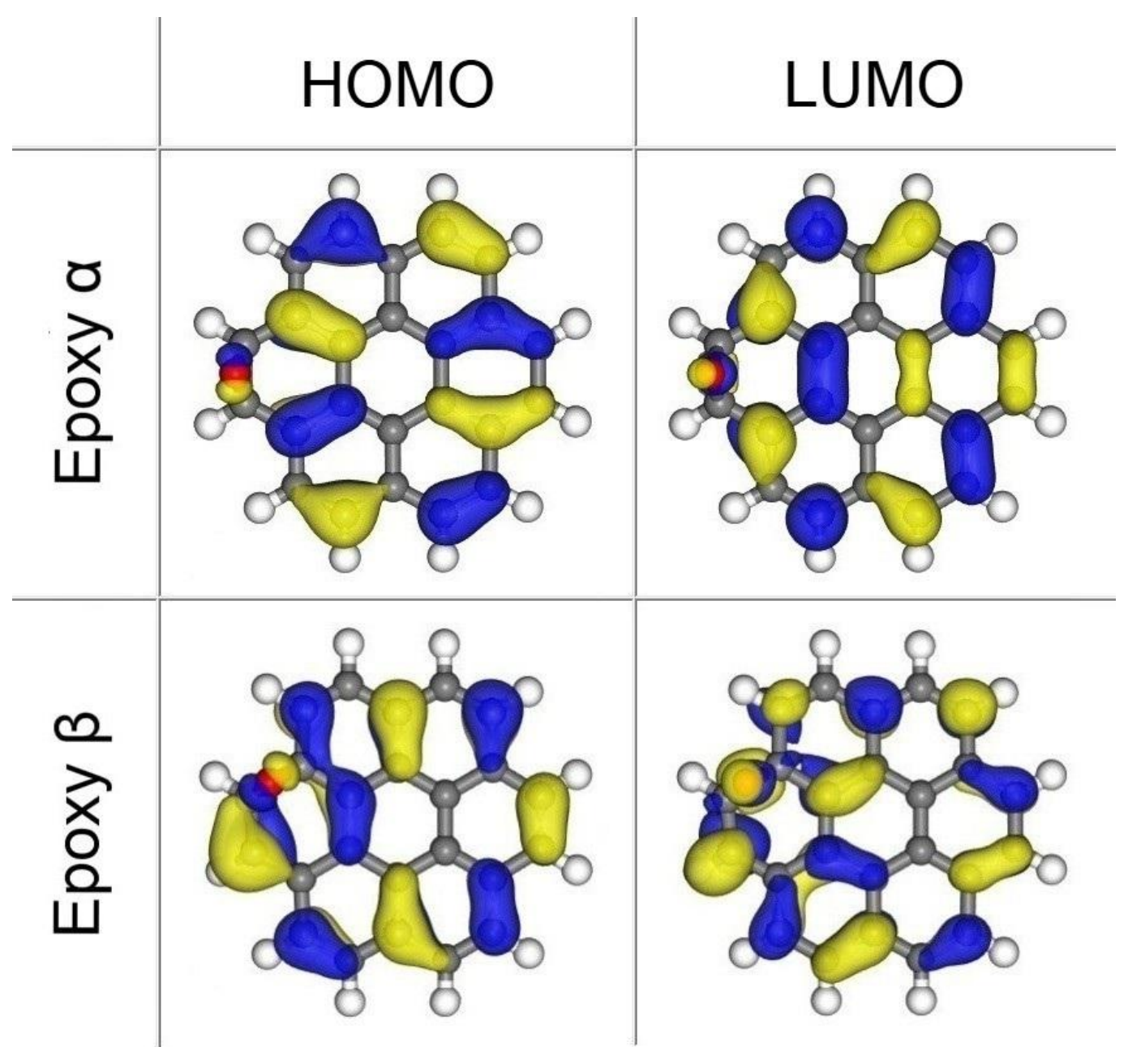
Epoxidation of coronene alters its structural characteristics, significantly influencing electronic and optical properties. Notably, the α-position exhibits minimal influence on both structural and optical characteristics. In contrast to the α-position, the epoxy group at the β-position exerts a significant influence on the final characteristics of coronene. The attachment of the oxygen atom induces localization of π-electrons within the epoxidized ring as well as two adjacent six-membered rings, thereby disrupting their delocalization and conjugation. Consequently, coronene epoxidized at the β-position exhibits a more pronounced redistribution of the frontier molecular orbitals (FMOs) compared to the α-position.



Spatial Distribution of Frontier Molecular Orbitals

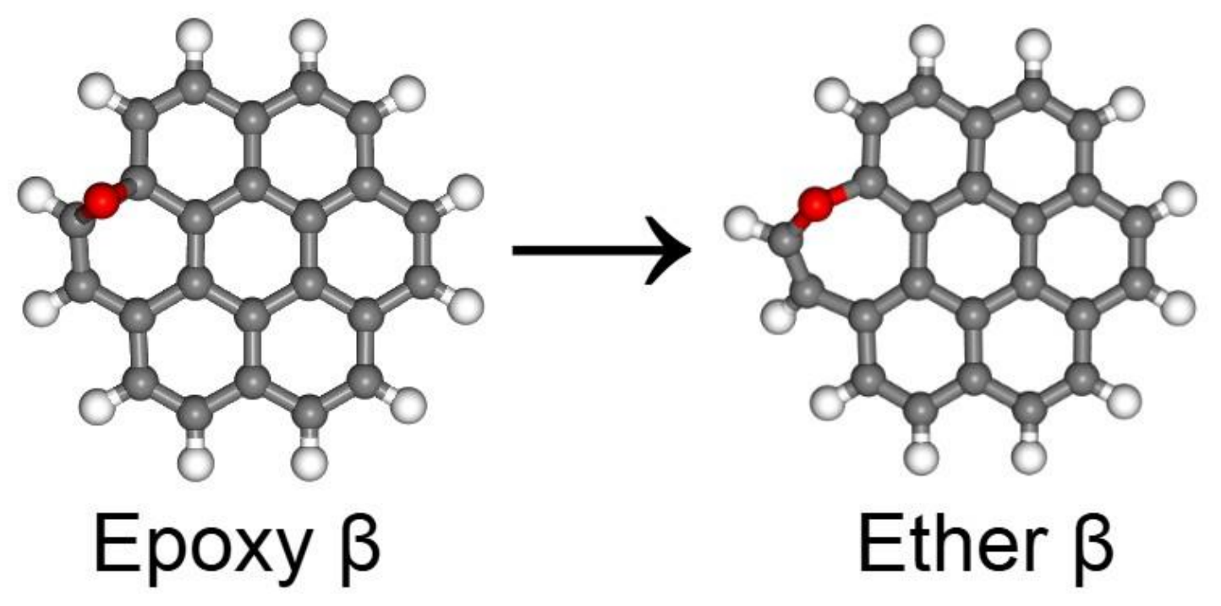
Epoxidation of coronene at the α-position does not induce significant redistribution of the FMOs. The most prominent effect of epoxidation is the slight shift of electron density of the HOMO and LUMO on the oxygen atom. Epoxidation of coronene results in symmetry breaking of the molecular structure, lifts the degeneracy of the HOMO/LUMO levels, and removes the symmetry-based forbidden character of $S_0 \rightarrow S_2$ transition.

The β-epoxy group significantly influences coronene's properties. LUMO density localization on the oxygen atom and adjacent bonds substantially narrows the energy gap, causing a bathochromic shift of absorption and emission bands. Symmetry breaking enhances HOMO-LUMO wave function overlap, increasing the transition matrix element for the $S_0 \leftrightarrow S_1$ transition.

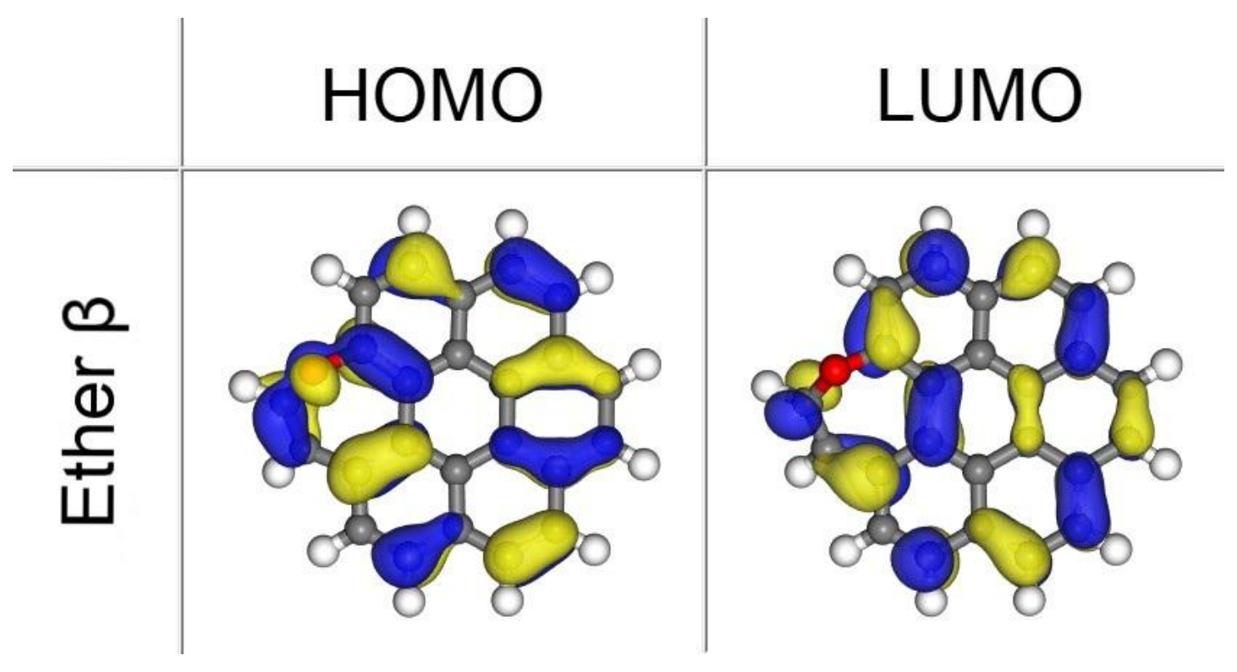


The metastability at the β-Position

Thermo-activation of epoxidized coronene can induce structural changes. At the β-position, epoxy-to-ether bridge transformation restores π-electron delocalization, enhancing system stability. Transition state calculations support this: the low transformation barrier at the β-position (~0.1 kcal/mol for S_0) indicates metastability. Notably, the structure with intact C—C bonds exhibits a higher oscillator strength for the $S_0 \leftrightarrow S_1$ transitions. Although the practical utilization of this metastable structure is limited, it reveals the mechanism by which epoxidation could enhance optical properties.



Structure	Singlet excited state	Absorption edge (nm)	Oscillator Strength	Fluorescence (nm)	Oscillator strength
Ether β	S1	409	0.209	688	0.043
	S2	397	0.019	—	—
	S3	321	0.002	—	—



Why Does Epoxidation Enhance Luminescence?

Based on the obtained results, we have established a principle governing the efficiency of optical tuning of carbon nanostructures via epoxidation. It is demonstrated that the critical factor is not the mere fact of functionalization, but rather its impact on the electron density. It was established that the possible luminescence enhancement is attributed to a substantial redistribution of the frontier molecular orbitals. These findings open up prospects for the development of photoluminescent materials for applications in optoelectronics, sensing, and biomedical imaging.

The full version of this study is available as a preprint on Zenodo.org. You can access it by scanning the QR code and following the provided link. We also plan to submit the final version to one of the MDPI journals in the near future and would be glad if you could read it upon publication.

If your research requires theoretical support or DFT-based calculations, we would be glad to help. Feel free to contact us at: dromanov@donstu.ru. Let's unravel the puzzles of chemistry together!

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