

Structural modification of graphitic carbon nitride (g-C₃N₄) to enhance the photocatalytic efficiency: A physicochemical and spectral study

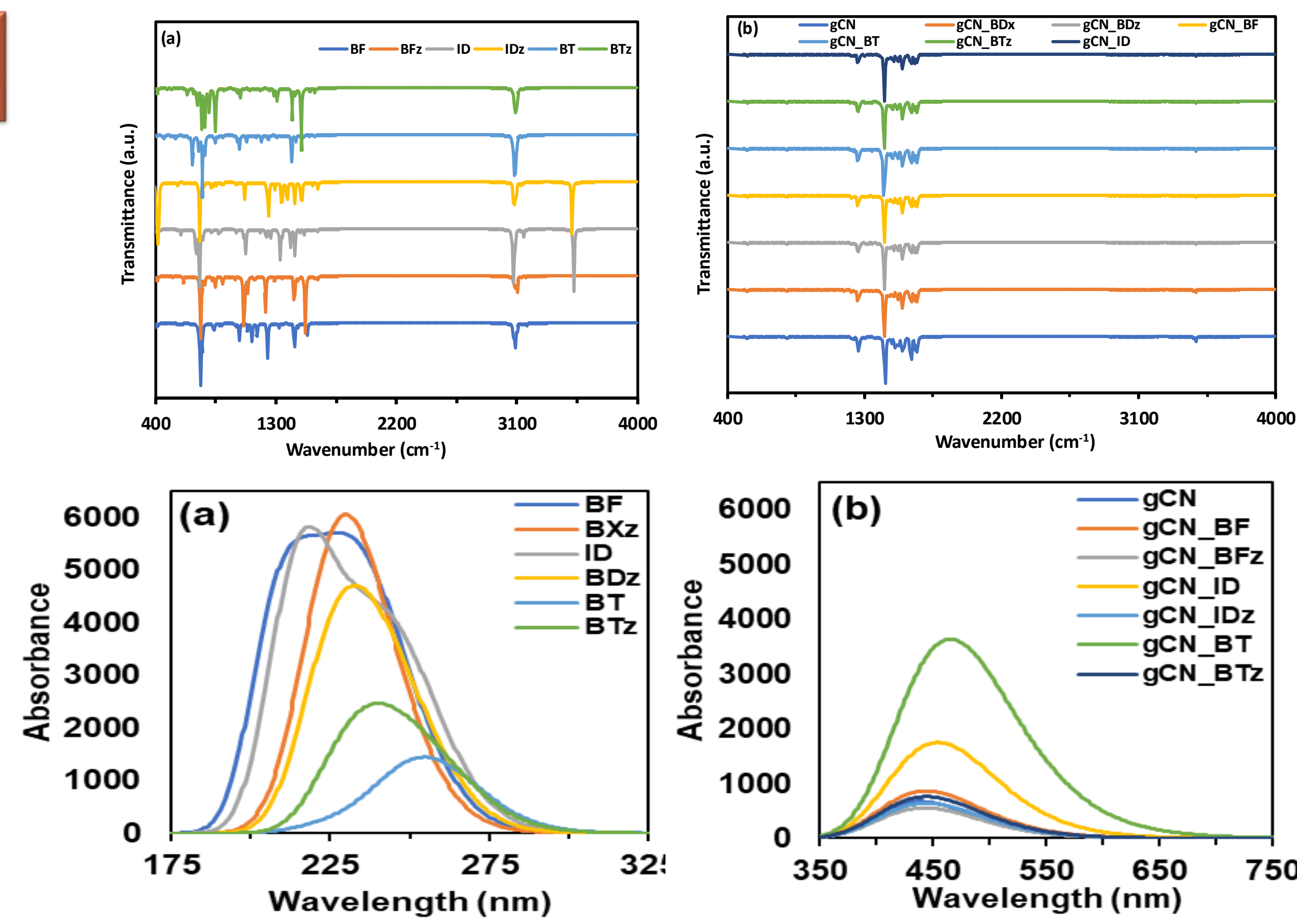
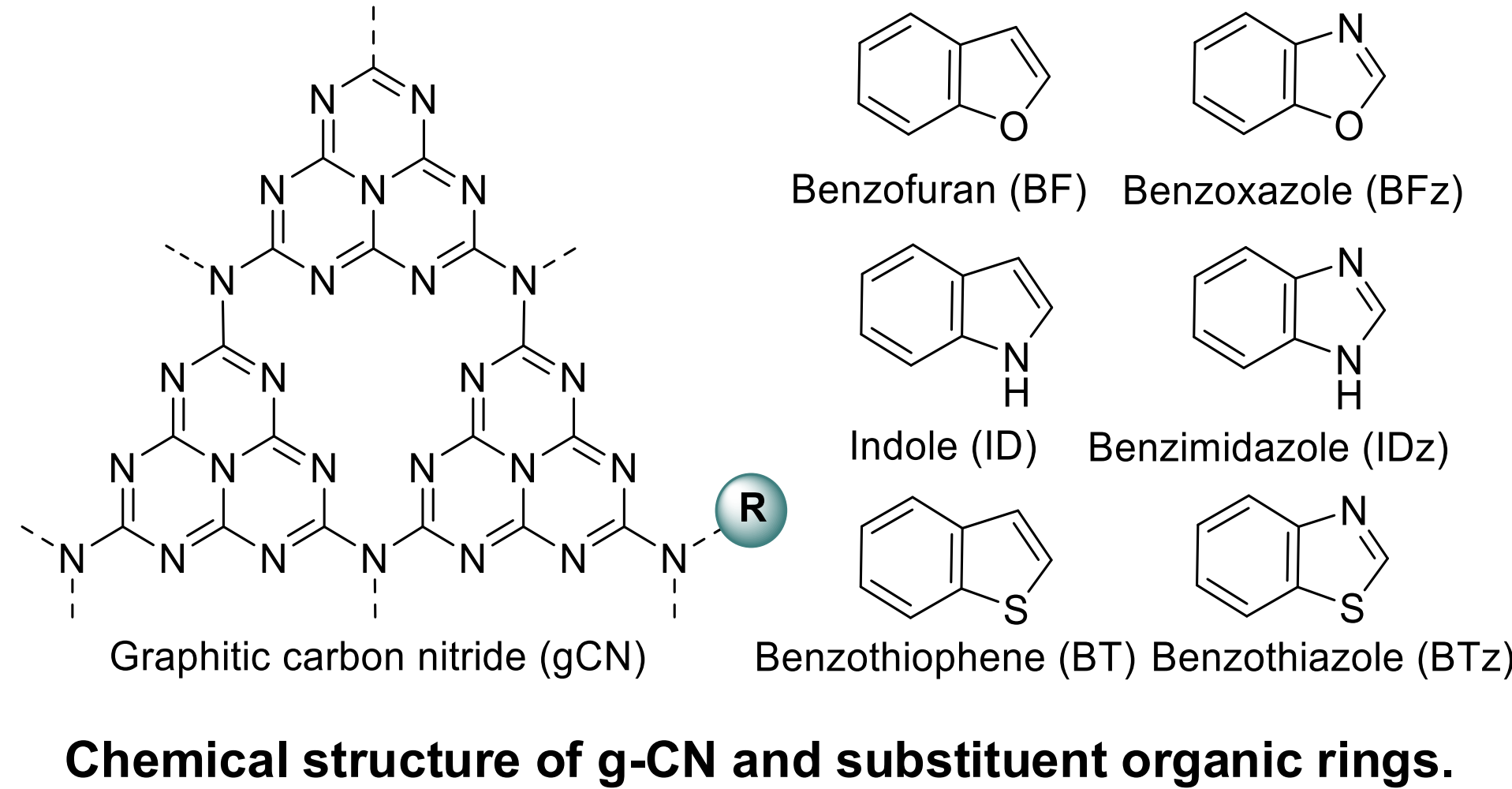
Mohammed Sakib Musa^{1*}, Mst. Farhana Afrin², Monir Uzzaman^{2*}

¹ Department of Applied Chemistry & Chemical Engineering, University of Chittagong, 4331, Bangladesh

² Department of Applied Chemistry, Mie University, Tsu, Mie 514-8507, Japan.

INTRODUCTION & AIM

Graphitic carbon nitride (g-CN), a metal-free, two-dimensional π -conjugated polymer, has attracted attention since 2009 for its visible-light-driven hydrogen production. With a bandgap of ~ 2.7 eV, g-CN is responsive to visible light and thermochemically stable, with a band structure suitable for water redox reactions. However, its practical photocatalytic performance is hindered by low surface area high charge recombination rates, and limited visible light utilization. To address these issues, structural modifications—particularly the introduction of intramolecular donor-acceptor (D-A) structures via elemental doping—have shown promise. Precursors such as BF, BFz, ID, IDz, and BTz serve as electron donors, enabling electron transfer to the g-CN framework upon excitation and facilitating D-A structure formation. These modifications are anticipated to improve charge separation and transport, thereby enhancing photocatalytic efficiency. This study investigates the potential of D-A modified g-CN using a theoretical framework to optimize its photocatalytic performance.



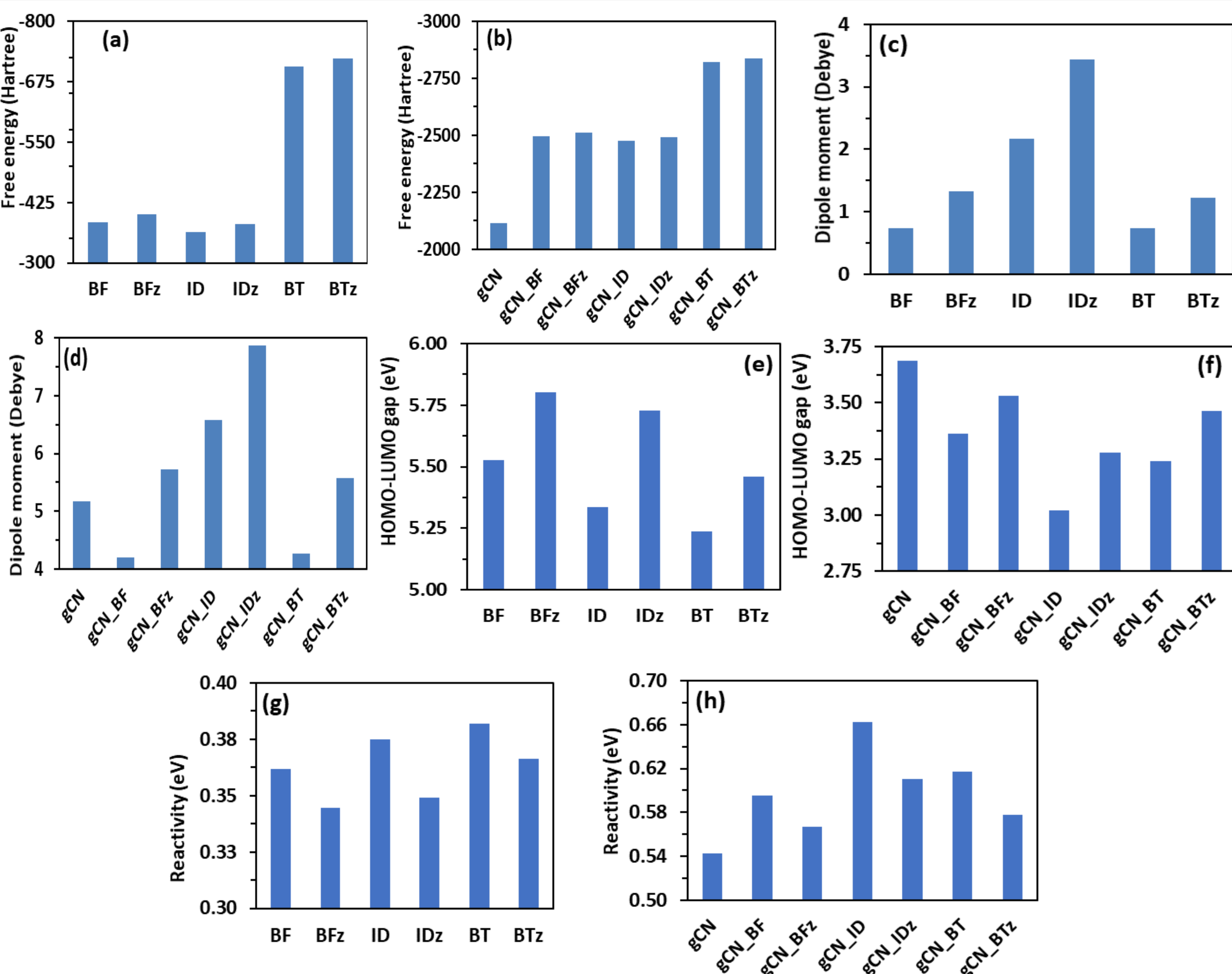
Theoretical FT-IR confirms grafting via new C–N vibrational modes. Absence of imaginary frequency confirms the structural stability of the modified g-CN.

The UV–vis absorption spectra exhibit a redshift for the modified g-C₃N₄ systems, particularly gCN-BT and gCN-ID, correlating with narrowed bandgaps. This spectral shift aligns with enhanced visible-light absorption, thereby reinforcing their potential as efficient photocatalysts.

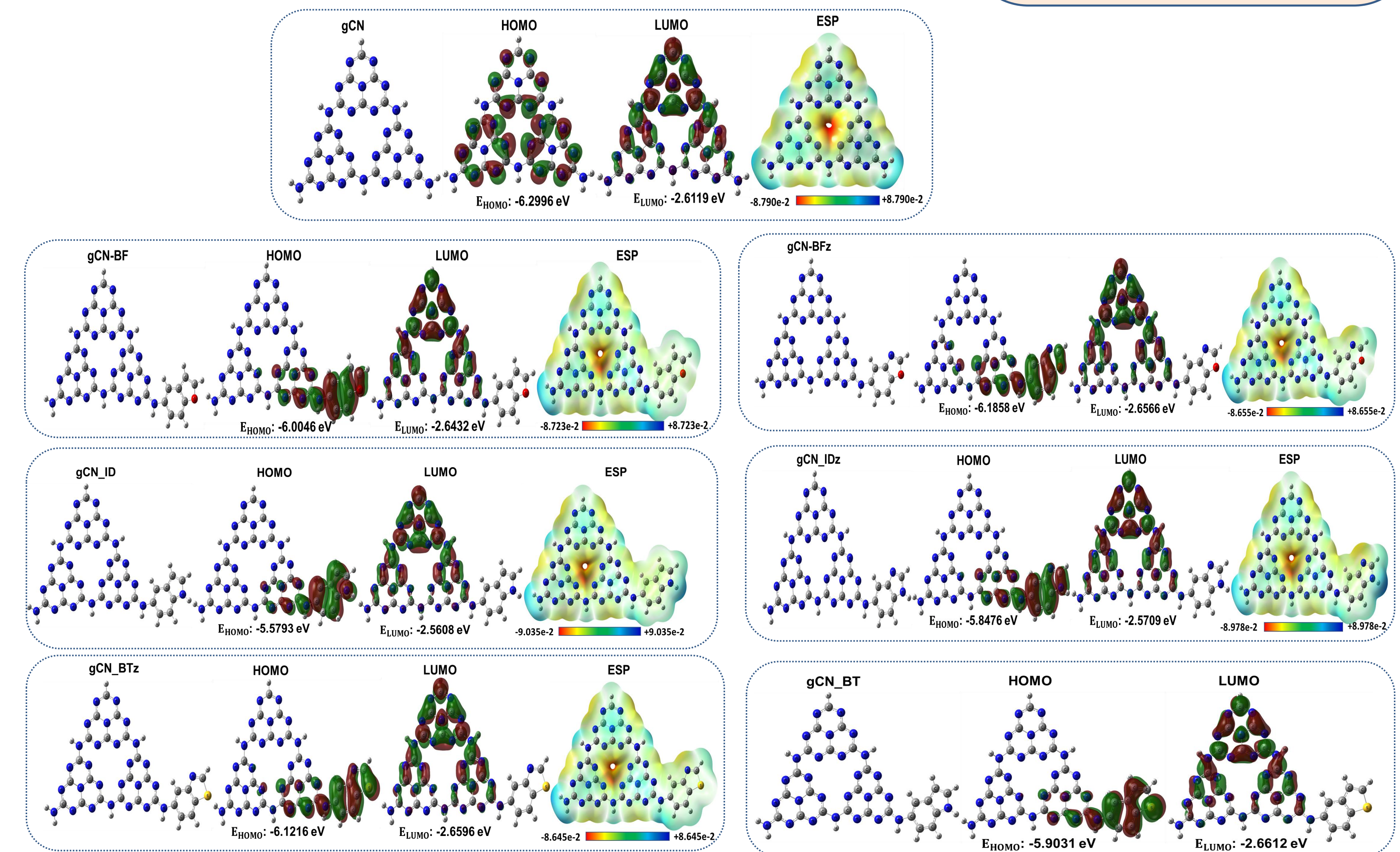
METHOD

Electronic structure and excited-state properties were computed using **density functional theory (DFT)** and **time-dependent DFT (TD-DFT)**. The hybrid **B3LYP functional** with the **6-31g(d)** basis set was employed to balance accuracy and computational efficiency for geometry optimization, energy calculation, and spectral analyses. Ground-state calculations (DFT) probed thermodynamic stability, HOMO-LUMO gaps, and dipole moments, while TD-DFT modeled UV-vis absorption spectra. **Gaussian 16** executed all quantum calculations, and **Multiwfn** analyzed wavefunctions for density of states (DOS).

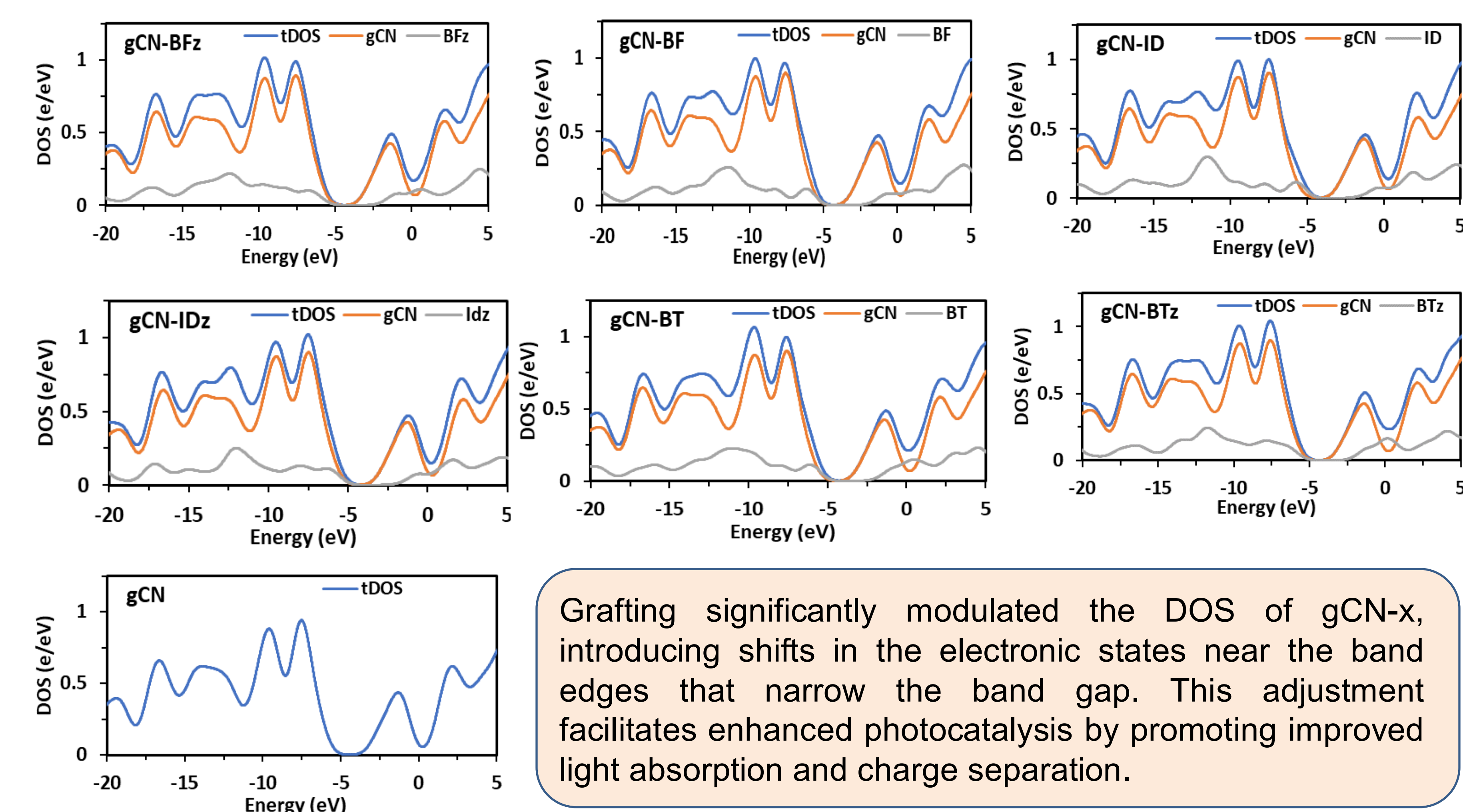
RESULTS & DISCUSSION



The figures (a-h) reveal that grafting agents (BF, BFz, ID, IDz, BT, BTz) induce substantial modifications in g-C₃N₄ thermodynamics and electronic properties. Changes in free energy across the grafted derivatives indicate enhanced binding affinity compared to pristine g-C₃N₄, with modified materials exhibiting more favorable thermodynamic profiles. Frontier molecular orbital analyses demonstrate reduced HOMO-LUMO gaps upon functionalization, which suggests improved charge separation and reactivity. Increased dipole moments in grafted samples reinforce improved charge transfer properties, which are critical for effective photocatalysis.



In pristine graphitic carbon nitride (gCN), the symmetric heptazine framework exhibits negligible charge polarization. However, upon functionalization with substituents such as BF, BFz, ID, IDz, BT, and BTz, a pronounced redistribution of electron density occurs. In these systems, the ground state electron density becomes predominantly localized on the grafted (donor) sites, whereas upon excitation, electrons are transferred to the carbon nitride framework, which serves as an electron acceptor. This obvious charge separation establishes an intrinsic electric field directed from the donor grafts to the acceptor carbon nitride matrix, thereby potentially augmenting photocatalytic performance.



Grafting significantly modulated the DOS of gCN-x, introducing shifts in the electronic states near the band edges that narrow the band gap. This adjustment facilitates enhanced photocatalysis by promoting improved light absorption and charge separation.

REFERENCES

1) Watanabe, Shigen, et al. "One pot synthesis of donor-acceptor carbon nitride with distinct thiophene rings accelerate photocatalytic hydrogen evolution." *Optical Materials* 158 (2025): 116482.

CONCLUSION

These findings underscore the value of incorporating donor-acceptor structures into graphitic carbon nitride, demonstrating the potential of molecular design in advancing efficient photocatalyst development.