CARBON NANOPARTICLES AS BIOMOLECULAR SENSORS

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INTRODUCTION

Carbon nanostructures — fullerenes, graphene, and nanotubes — owing to their high conductivity, large surface area, and stability, find applications in electronics, photonics, medicine, and energy technologies [1].

Graphene and nanotubes, due to π–π interactions and efficient charge transfer, serve as promising platforms for nanocomposites [2].

Complexes of these nanomaterials with photosensitive dyes combine the optical properties of organic molecules with the electronic characteristics of nanostructures, which is important for photodynamic therapy, organic solar cells, and biosensors [3].

Fullerenes C_{60} and C_{70} are distinguished by their high electron affinity; C_{70} exhibits a broader absorption spectrum in the visible range and a higher ability to generate singlet oxygen [4]. Polymethine dyes, characterized by intense and narrow absorption bands, form charge-transfer complexes with carbon nanostructures, resulting in modified spectral properties [5].

The aim of this work is to investigate the spectral properties of complexes of organic dyes with fullerenes C_{60} and C_{70}, graphene sheets, and nanotubes, as well as to model the electronic structure of such systems.

EXPERIMENTAL

Figure 4 shows examples of the investigated samples prepared by the Langmuir–Blodgett and spin-coating methods.

The absorption spectra reveal that the main peak at 682 nm corresponds to the HOMO→LUMO transition of the polymethine chain, which lies within the phototherapeutic window.

The fullerene C_{60} film exhibits peaks at 330 and 420 nm, attributed to π→π* transitions, similar to the absorption features of nanotubes in the UV region.

Upon interaction of the dye with the nanostructures, a shift of the absorption maximum is observed: to 680 nm for fullerenes and to 667 nm for nanotubes.

For the nanotube–dye complex, broadening and increased intensity of the short-wavelength shoulder are also noted.

SEM images of the nanotube film are presented in Fig. 9.

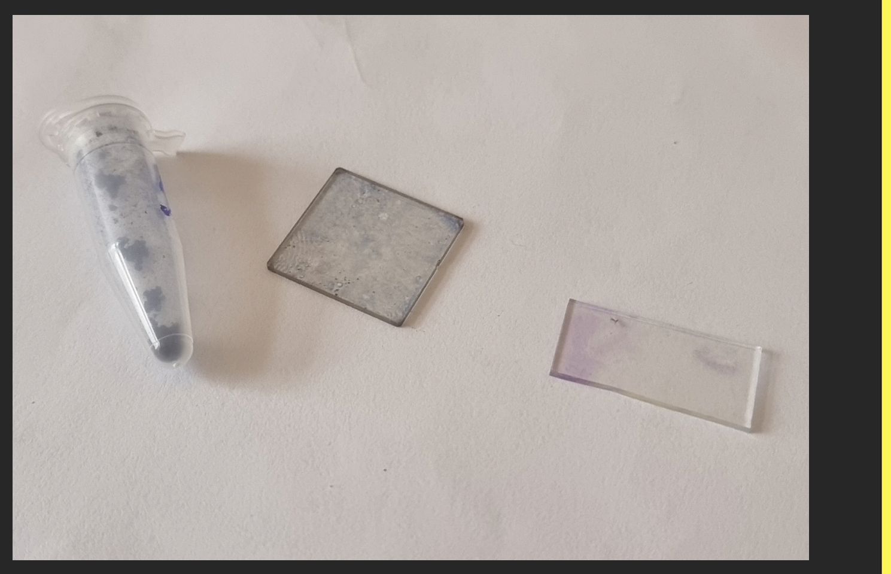


Fig. 4. Dye solution (test tube) and two samples (films) prepared by Langmuir–Blodgett and spin-coating methods.

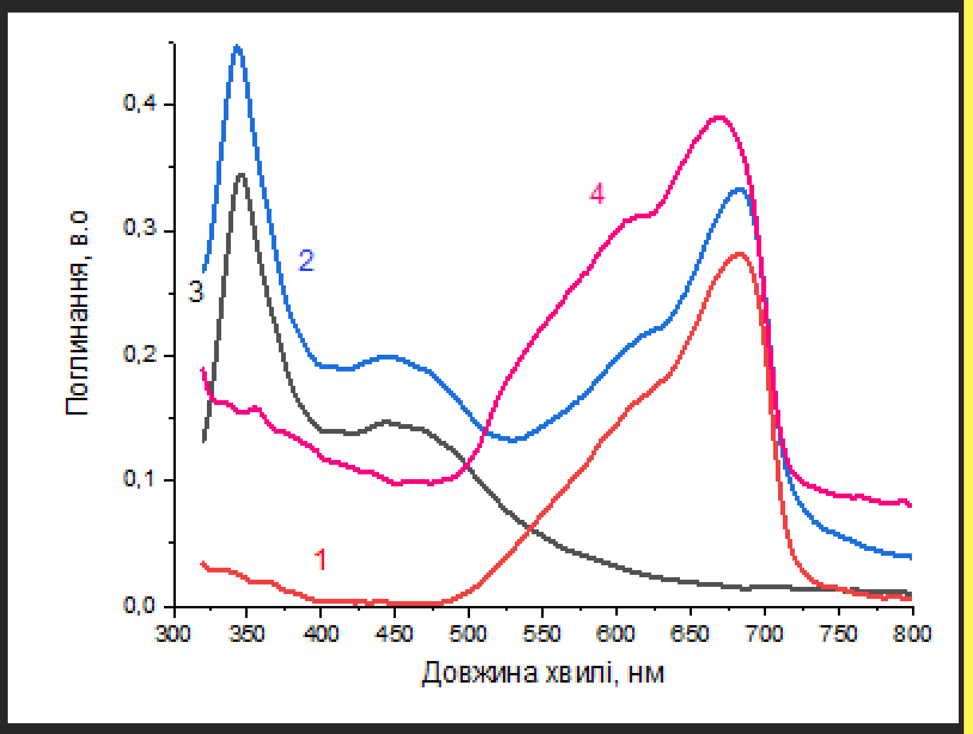


Fig. 5. Normalized optical absorption spectra of dye film (1), fullerene C_{60}–dye film (2), fullerene film (3), and nanotube–dye film (4). Substrate: quartz; films prepared from dichloromethane solution. Film thickness: d = 50 nm.

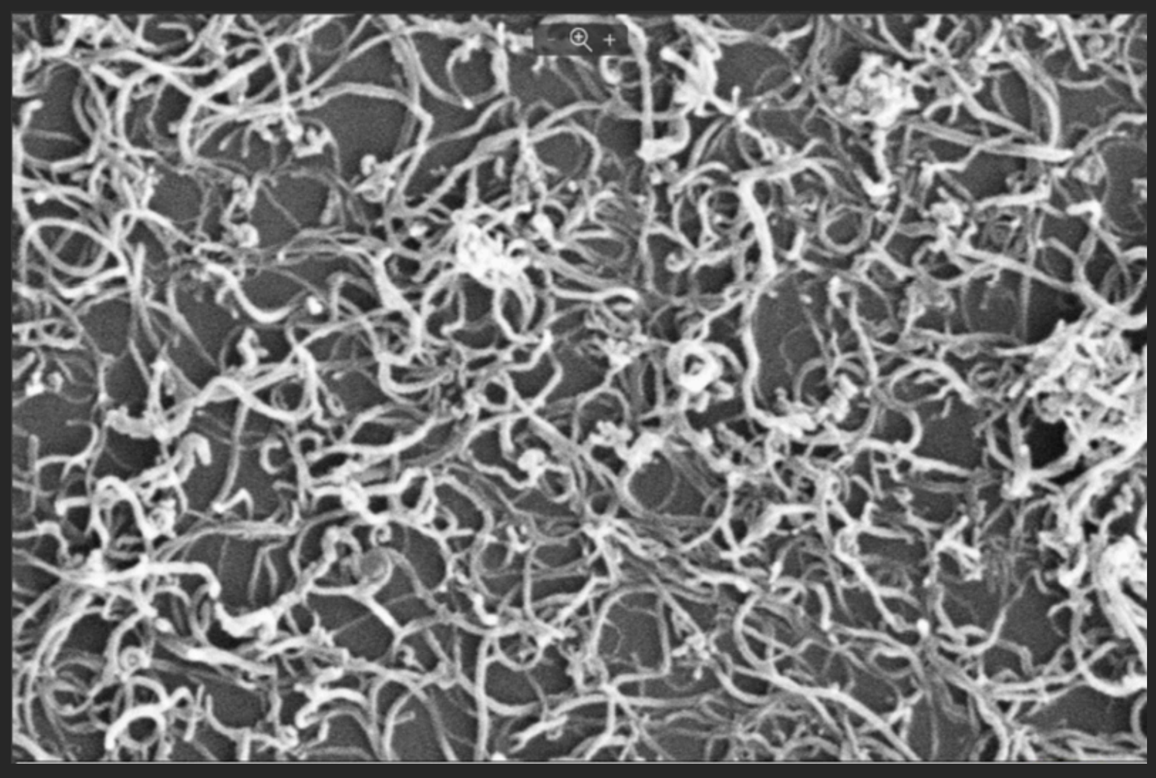
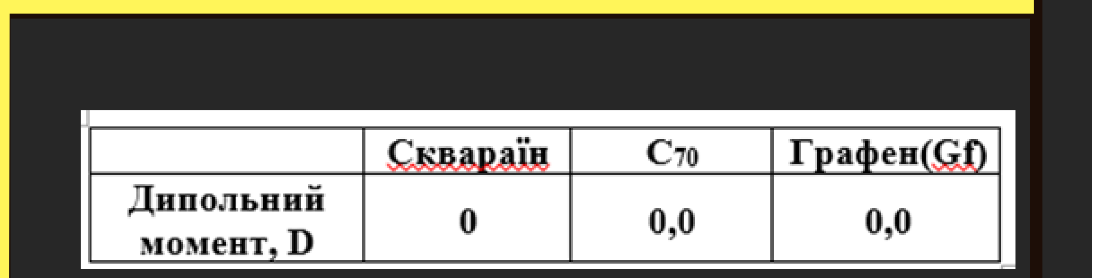
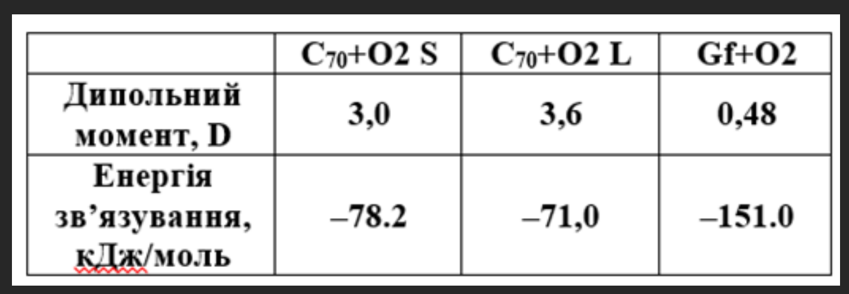


Fig. 9. Scanning electron microscopy (SEM) images of multi-walled carbon nanotube films functionalized with dyes.



	Скваraїн	C_{70}	Графен(Gf)
Дипольний момент, D	0	0,0	0,0

Table 1. Dipole moments of individual molecules.



	C_{70}+O2 S	C_{70}+O2 L	Gf+O2
Дипольний момент, D	3,0	3,6	0,48
Енергія зв'язування, кДж/моль	–78.2	–71,0	–151.0

Table 2. Calculated dipole moments and binding energies for the studied complexes.

CALCULATIONS

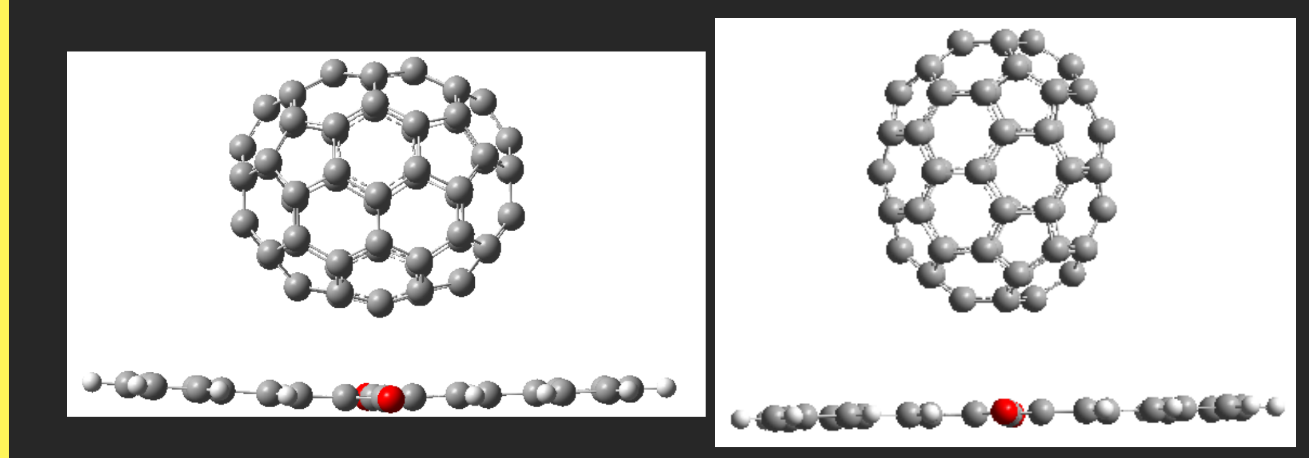


Fig. 1. Variants of dye orientation relative to the fullerene.

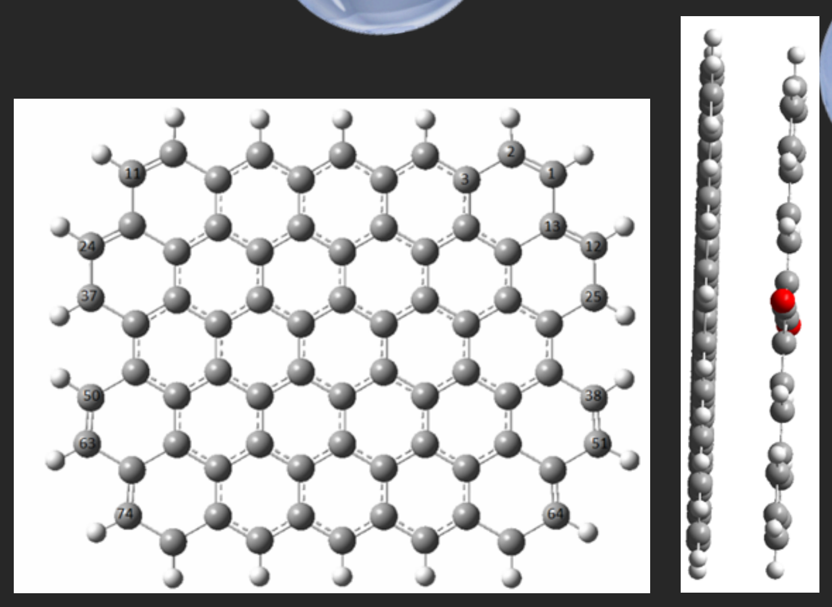


Fig. 2. Graphene sheet and its complex with the dye.

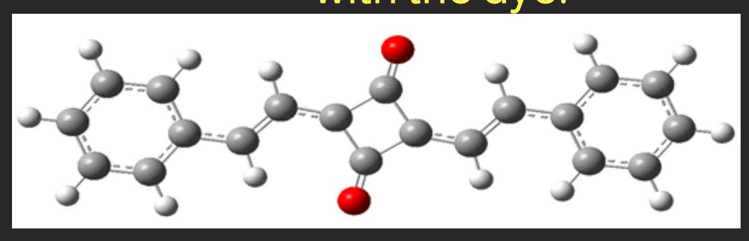


Fig. 3. Squaraine dye molecule.

To investigate the structural and energetic characteristics of the squaraine dye (O_2) complexes with fullerene C_{70}, quantum-chemical calculations were performed using Gaussian 09 with the WB97XD functional and the 6-31G(d) basis set. The chosen functional accounts for dispersion interactions and effectively models van der Waals forces and π–π stacking.

The modeling was carried out for two orientations: L — with the dye oriented perpendicular to the long axis of C_{70}, and S — perpendicular to the short axis (Fig. 2.3). The initial intermolecular distance was set to approximately 3.4 Å. All calculations were performed in the gas phase with full geometry optimization and without symmetry constraints.

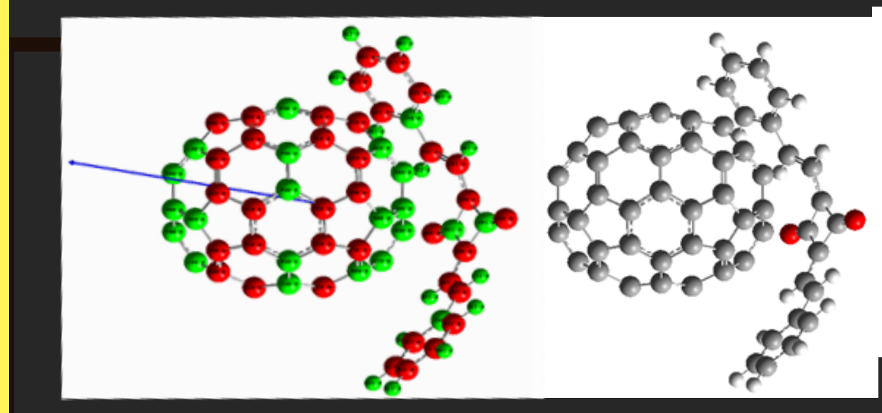


Fig. 6. Optimized geometry and charge distribution of the C_{70} fullerene complexes with squaraine dye in the case of localization near the larger diameter (L) of the C_{70} fullerene.

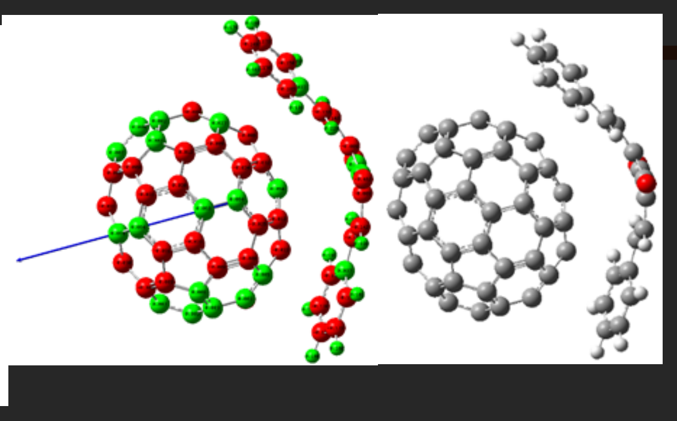


Fig. 7. Optimized geometry and charge distribution of the C_{70} fullerene complexes with squaraine dye in the case of localization near the shorter diameter (S) of the C_{70} fullerene.

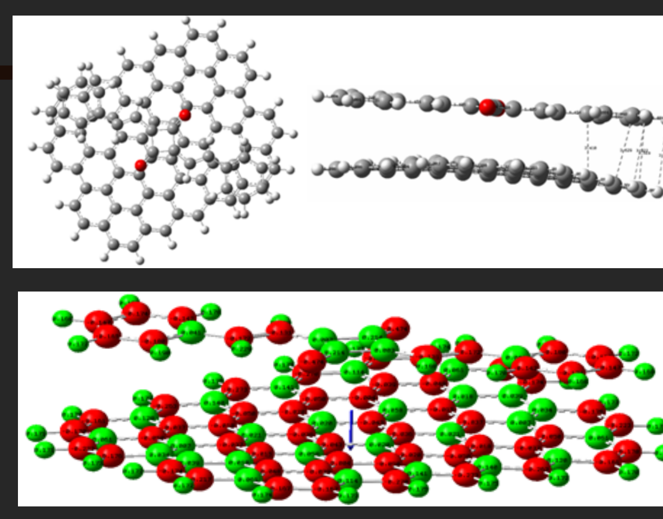


Fig. 8. Optimized geometry and charge distribution of the graphene sheet complex with squaraine dye, including the dipole moment of the complex.

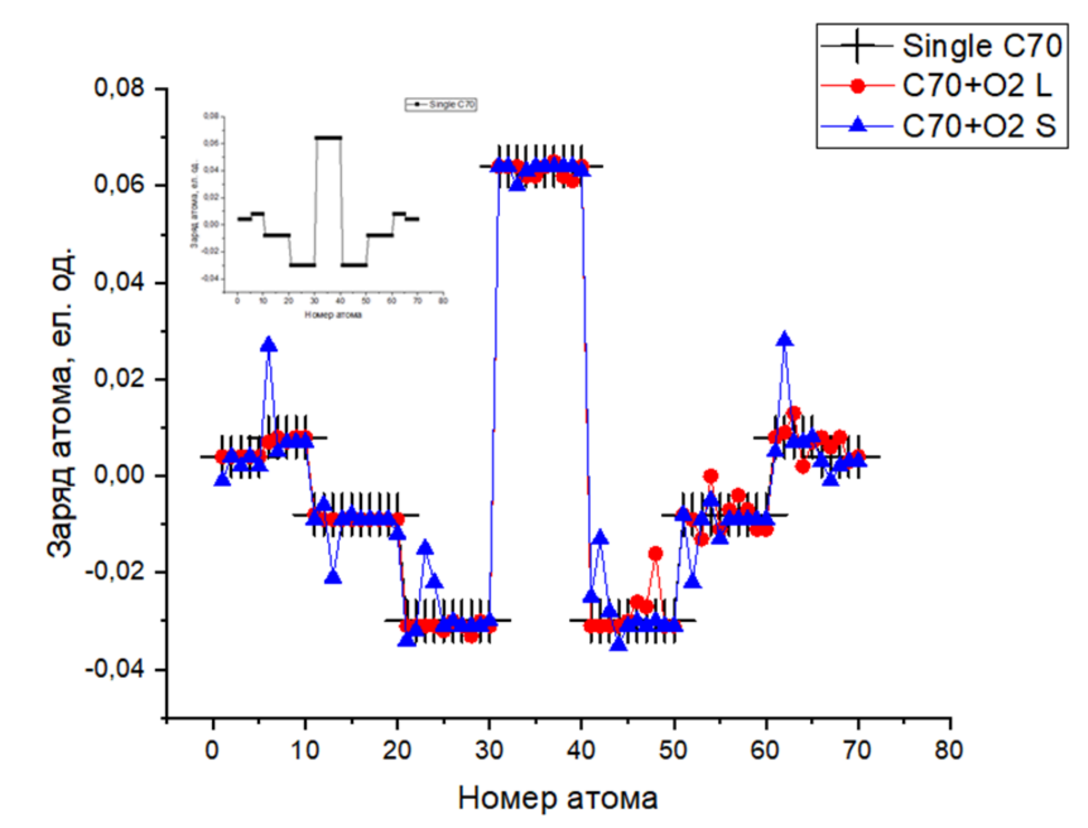


Fig. 10. Charge distribution of the pristine C_{70} fullerene and its complexes with squaraine dye in two localization configurations (S and L).

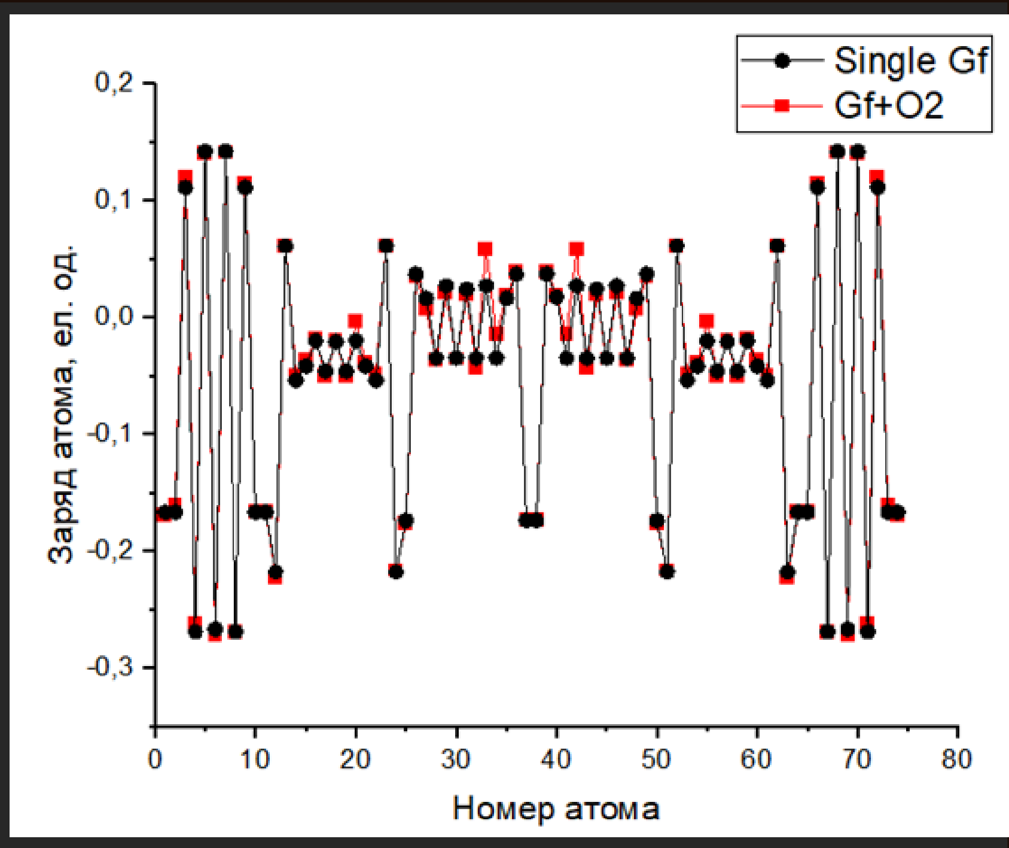


Fig. 11. Charge distribution of the graphene sheet (Gf) without complexation and in complexes with squaraine dye.

Conclusions

1. During the formation of films of squaraine dyes with carbon nanostructures possessing different degrees of carbon atom hybridization, deposited by solution casting, a transformation of the electronic structure of the complexes occurs. This is accompanied by changes in the electronic band gap, as evidenced by shifts of the absorption maxima towards shorter wavelengths—up to 680 nm for fullerenes and up to 667 nm for nanotubes compared to the dye films (Fig. 5).

2. According to quantum-chemical calculations, stable complexes are formed upon interaction of squaraine dyes with carbon nanostructures of varying carbon atom hybridization. The highest binding energies are characteristic of:

1) graphene sheet and squaraine dye: −151 kJ/mol
2) C_{70} fullerene and squaraine dye (S-localization): −78 kJ/mol
3) C_{70} fullerene and squaraine dye (L-localization): −70.8 kJ/mol

The stability of these complexes is attributed to donor–acceptor interactions, where the dye acts as an electron donor and the carbon nanostructure as an acceptor. This is supported by charge redistribution, the emergence of a dipole moment, changes in the energy band gap levels, and π–π stacking interactions.

3. As a result of the interaction between the squaraine dye and carbon nanostructures, a redistribution of molecular orbital energies occurs, leading to the formation of new molecular orbitals localized simultaneously on both components of the complexes. Consequently, the HOMO and LUMO levels of the dye, responsible for absorption in the phototherapeutic window, shift towards shorter wavelengths by:

1) 1.4% for the graphene sheet–squaraine dye complex
2) 4.6% for the C_{70} fullerene–squaraine dye complex (S-localization)
3) 3.8% for the C_{70} fullerene–squaraine dye complex (L-localization)

References:

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