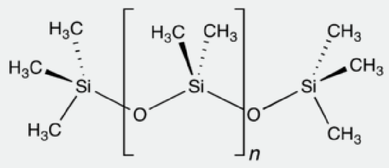
DFT simulations of aliphatic and aromatic polydimethylsiloxane - interacting with graphene sheet

D. A. Kalchevski[1], S. K. Kolev[1], D. Trifonov[1], K. V. Ivanov[2], D. A. Dimov[1], Yan Yan[2], D.S. Benkova[3], A. S. Kostadinova[3] and T. I. Milenov[1]

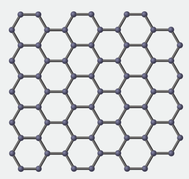
[1]"Acad. E. Djakov" Institute of Electronics, Bulgarian Academy of Science, Sofia 1784, Bulgaria
[2] Shenzhen Institute of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055, China
[3] Institute of Biophysics and Biomedical Engineering, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

Background and aim of the study



Polydimethylsiloxane

- ✓ Dielectric properties
- ✓ Hydrophobicity
- ✓ Biocompatibility,
- ✓ Thermal stability
- ✓ Optically transparency
- ✓ Excellent interfacial bonding capacities



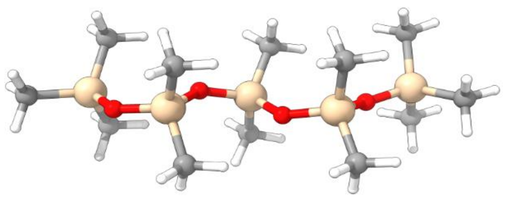
Graphene

- ✓ Extraordinary electrical properties
- ✓ Biocompatibility
- ✓ Well-established mass production methods
- ✓ High tensile strength
- ✓ High-charge carrier mobility
- ✓ High heat conduction capability

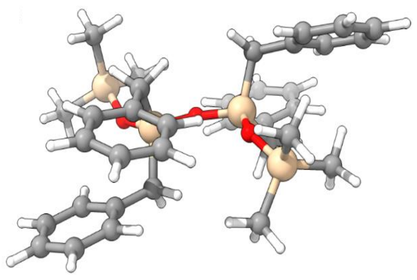
Graphene/PDMS-based sensors hold immense potential for utilization in contemporary biomedicine. They can be crafted for specific wearable sensing, electrochemical, and strain-sensing applications to monitor physiological signals and selected parameters of the human body.

This study models the adsorption of two siloxane polymers - methyl group terminated, a 5-membered oligomer of polydimethylsiloxane (**5DMS**) and methyl group terminated, a 2-membered oligomer of poly(dimethylsiloxane-co- dibenzylsiloxane) (**2DMS2DBS**) - on a graphene substrate through ab initio density functional calculations. The focus is on complex responses of the electronic structure and the associated properties, which experimental determination is too expensive to impossible[1,2].

Methodologies and Results

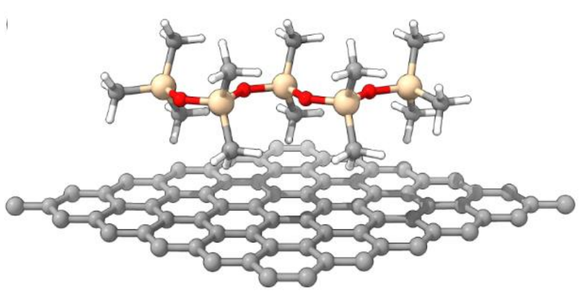


Optimized geometry of **5DMS** in vacuo.

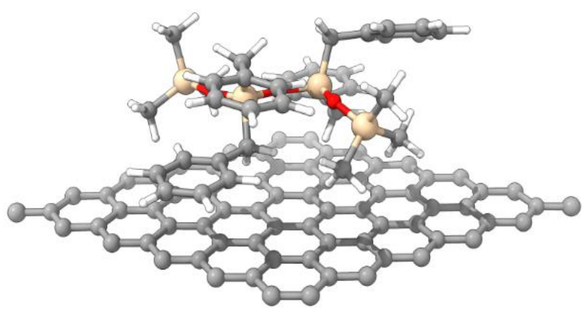


Optimized geometry of **2DMS2DBS** in vacuo.

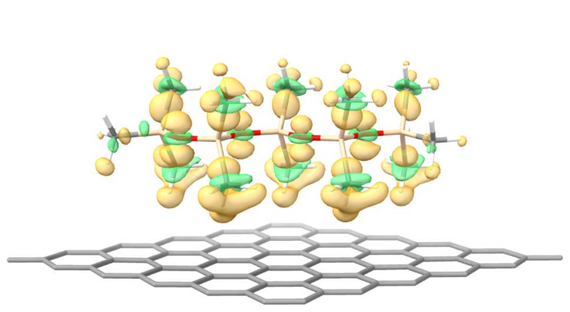
- Calculations were performed using the CP2K/Quickstep package. The Self-Consistent Field (SCF) optimizations were conducted at the Density Functional Theory (DFT) level, utilizing the Generalized Gradient Approximation (GGA) functional Perdew-Burke-Ernzerhof (PBE). The double-zeta quality basis set DZVP-MOLOPT-SR-GTH, optimized for gas and condensed phase system properties, is applied to all atoms.
- The electronic wave function was expanded using the Gaussian Plane Wave (GPW) method. Explicit modeling was limited to valence electrons, while core electronic shells were represented by Goedecker-Teter-Hutter (GTH) pseudopotentials, optimized for PBE. A charge density cutoff of 400 Rydberg (Ry) was used for the finest grid level, with a total of five multigrids employed to enhance calculation efficiency
- All systems were modeled using the unrestricted Kohn-Sham formalism. Dispersion interactions were included in all calculations using the latest D3 revision of the DFT + D method, which incorporates three-body terms for improved accuracy.
- Periodic Boundary Conditions (PBC) were applied when appropriate. All structures depicted were optimized geometrically. Post-optimization, the energetic effects of adsorption were determined by comparing the energy differences between isolated adsorbate, isolated adsorbent, and their respective complexes.
- Localized Orbital Locator (LOL) plots were generated using the Multiwfn program, providing insights into the electronic structure and bonding characteristics of the systems studied.



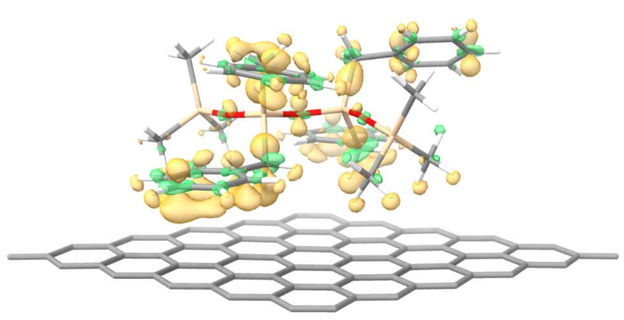
The optimized geometry of the complex **G_5DMS** (Graphene and 5DMS) with hexagonal PBC cells.



The complex **G_2DMS2DBS** (Graphene and 2DMS2DBS) optimized geometry with hexagonal PBC cells.

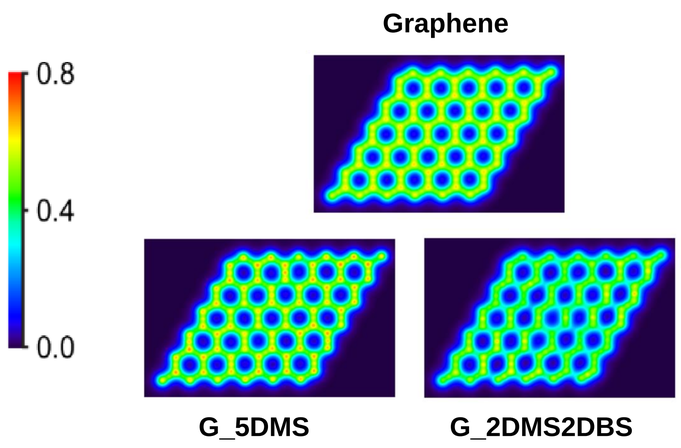


Electronic density difference due to adsorption of **5DMS** oligomer onto graphene. The contour is at isovalue 0.0015.

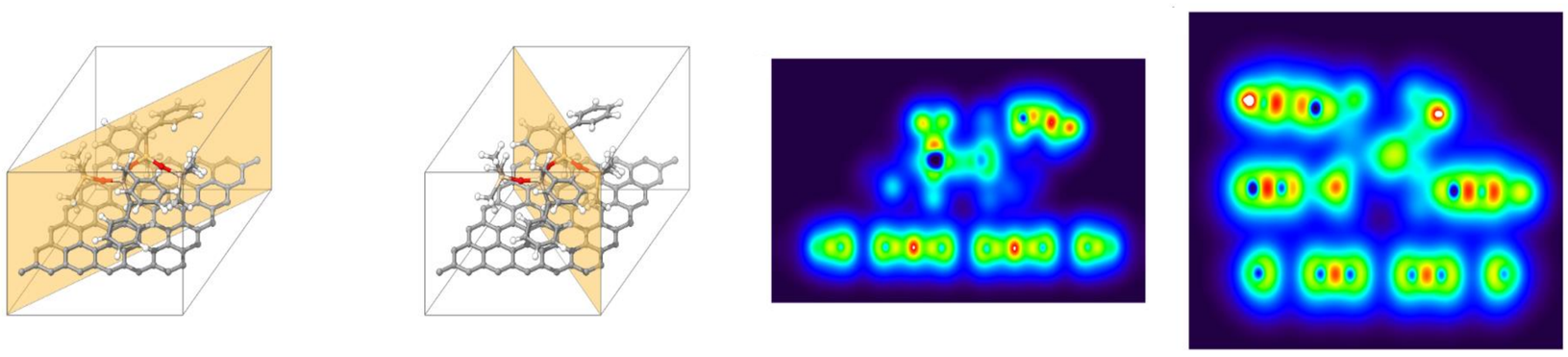


Electronic density difference due to adsorption of **2DMS2DBS** oligomer onto graphene. The contour is at isovalue 0.0015.

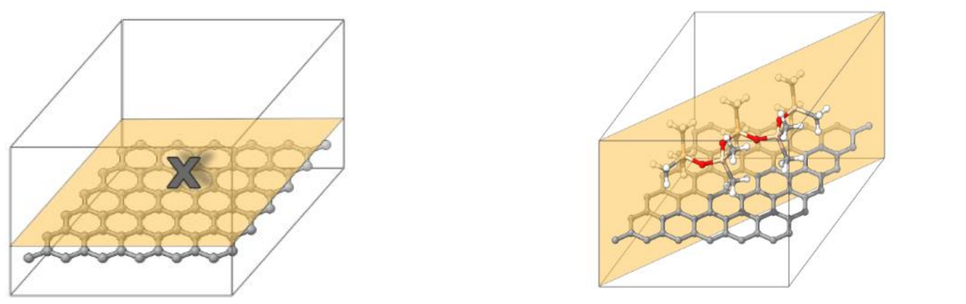
π-LOL plot over the graphene plane

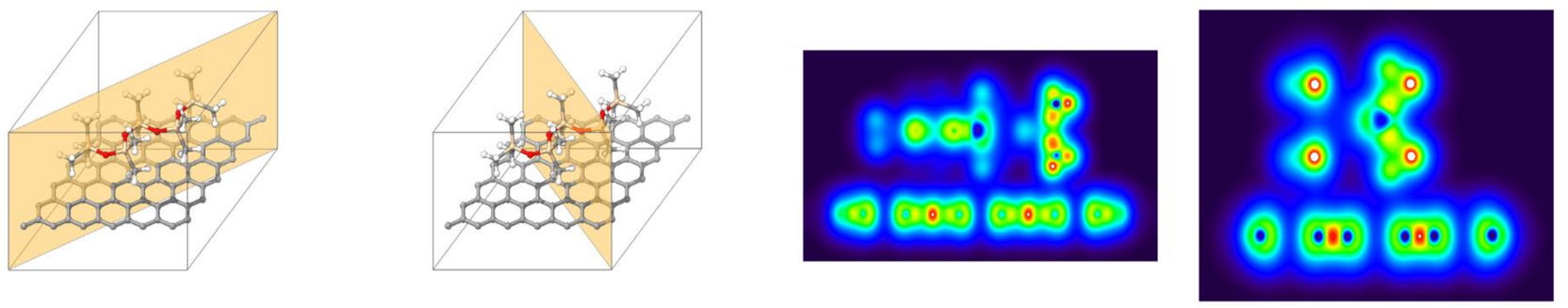


LOL plots of the G_2DMS2DBS complex in planes illustrated below the corresponding plots



LOL plots of the G_5DMS complex in planes illustrated below the corresponding plots





Conclusions

The adsorption of two siloxane-based polymers on graphene was modeled with the GGA density functional PBE. 5DMS interacts with the adsorbent only through aliphatic groups, while the 2DMS2DBS other also engages in aromatic π-π stacking. The adsorbates are modeled as methyl-terminated oligomers. The structures of the chain fragments and the graphene sheet are optimized separately and in a state of adsorption. In the π-π complex two of the four aromatic rings of the ligand reorient for intermolecular stacking with the graphene. The shortest distance between the aliphatic molecule and the adsorbent is 2.68 Å, while in the case of the aromatic one, that distance is 2.63 Å. The intermolecular binding of both adsorbents alters the shape of the graphene towards a more round one. The three-point angle between the two further-most carbon atoms and the center of the sheet changes from 0 ° to 6.57 ° in the presence of the aliphatic oligomer and 6.58 ° in the presence of the aromatic one. The difference in electronic density, arising from the adsorption is visualized for both systems. Localized orbital locator plots demonstrate a far more significant change in electronic distribution in the graphene sheet for the aromatic complex. The difference in interaction strength is most clearly visible in the energetic effect of adsorption. While the binding stabilization of the aliphatic oligomer is 61 kJ/mol (potential energy), the corresponding value for the π-π complex is comparable with the barrier height of typical organic reactions: 173 kJ/mol.

References

1. Hong, H.; Zhang, J.; Zhu, Y.; Tse, S.D.; Guo, H.; Lai, Y.; Xi, Y.; He, L.; Zhu, Z.; Yin, K.; Sun L.; In Situ Polymer-Solution-Processed Graphene–PDMS Nanocomposites for Application in Intracranial Pressure Sensors. Nanomaterials 2024, 14, 399.
2. Li, B.; Xianbin, Z.; SeHyun, K.; Xuhao, W.; Fuhao J.; Rong, L.; Sang Woo, J.; Chenhao C.; Xinlin L.; Fully Printed Non-Contact Touch Sensors Based on GCN/PDMS Composites: Enabling over-the-Bottom Detection, 3D Recognition, and Wireless Transmission. Science and Technology of Advanced Materials, 2024, 25.

Acknowledgments

The authors gratefully acknowledge the financial support of the Bulgarian Scientific Research Fund by grant No. KP 06-H77/13. The authors also acknowledge the provided access to the e-infrastructure of the NCHDC – part of the Bulgarian National Roadmap on RIs, with financial support by Grant No D01-168/28.07.2022.