

THz, Raman, and fluorescence characterization of a weak-bound complex of *h*BN and *trans*-stilbene

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1. Introduction

Hexagonal boron nitride (*h*BN) nanosheet is a 2D material, which is structural and isoelectronic analogue of graphene, but in contrast to the latter, *h*BN is an electrical insulator and does not absorb in the visible region [1]. Ultra-thin *h*BN is successfully applied as the dielectric layer in field effect transistors, protective cover in devices, buffer layer in film growth, etc. The properties of *h*BN nanosheets can be modified using the functionalization of their surface by molecular architectures. Non-covalent functionalization of 2D *h*BN provides a way to modify the physical properties without violating its structure. Adsorbed molecules interact with surfaces due to relatively weak van der Waals interactions. Downsizing of 2D *h*BN nanosheet allows to production of *h*BN quantum dots, which have unique photophysical properties and are biocompatible that determines their promising application in biomedicine for the diagnosis of various diseases, bioimaging and targeted drug delivery [2]. Apparently, the *h*BN surface can form π - π staggered stacking interactions with organic molecules containing aromatic rings. Both problems mentioned require an understanding of the strength of interaction and its manifestations in different spectral ranges and techniques including IR, Raman, and fluorescence (FL) spectra. The THz range has unique features because low-frequency deformation vibrations of fragments of complex relatively each other that characterize their weak interaction, manifest namely in the THz range. The *trans*-stilbene (TST) molecule serves as a suitable simple candidate to reveal the features of the formation of the *h*BN surface complexes with organic molecules using spectroscopic and theoretical methods.

2. Experimental

The TST molecules were adsorbed on the *h*BN surface by solvation in chloroform and evaporation of the solvent. Then samples of pure TST, the complex of TST and *h*BN, and a mix of *h*BN and polyethylene were pressed to obtain tablets 0.8 mm thick for THz and FL measurements. The THz spectra were measured at room and liquid nitrogen temperatures in the range of 0.4–3.5 THz. The Raman spectra were measured for powder samples.

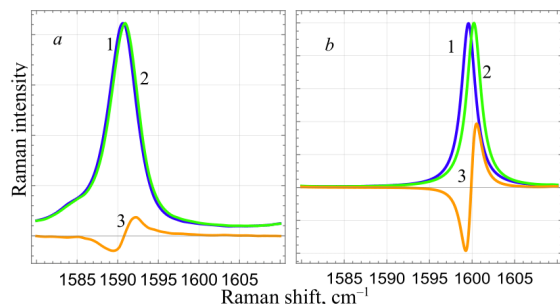


Fig. 1. Fragments of experimental (a) and theoretical (b) Raman spectra of TST (1), TST+*h*BN (2), and their difference (3).

complex demonstrates two additional weak bands at 0.7 and 1.1 THz compared to the spectrum of pure TST. These bands correspond to the librations of the TST molecules relative to the *h*BN surface. The formation of the complex also leads to a blue shift of mostly intensive Raman lines at 1639 (C=C stretching), 1591 (ring stretching), 1190 (C–ring stretching, Fig. 1), and 994 cm^{-1} (trigonal ring deformation) on $\sim 4 \text{ cm}^{-1}$. Both steady-state and time-resolved FL measurements also show the formation of the complex. The FL kinetic lifetime of the complex (0.917 ns) is shorter than pure TST (1.180 ns), but longer than pure *h*BN (0.440 ns).

5. Acknowledgements

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6. References

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3. Theoretical

The quantum chemical calculations of the structure and spectral characteristics of an isolated TST molecule, a hexagonal $\text{B}_{27}\text{N}_{27}\text{H}_{18}$ quantum dot, a complex of a quantum dot with TST molecule, as well as 2D *h*BN and 3D TST crystals, were performed at the DFT level of theory with PP-based plane wave basis sets for 2D and 3D crystal models and all-electron Gaussian basis sets for other models.

4. Results