Spectroscopic and theoretical insights into van der Waals interaction between organic compounds and hexagonal boron nitride

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Van der Waals (vdW) composites constructed from two-dimensional (2D) inorganic materials and organic compounds are the promising materials for various applications in electronics, photonics, bioimaging, target drug delivery, etc. One of the advantages of vdW complexes with respect to those bonded covalently is “fine-tuning” modification of the physical properties of their building blocks. One of the most promising 2D material in this context is hexagonal boron nitride (hBN), which is isoelectronic to graphene and has high chemical and thermal stability as well as thermal conductivity. For the practical purposes it is critically important to understand the hBN ability to interact with different organic compounds that can be effective light harvesters (as porphyrins), exhibit photoisomerization and/or optical properties highly dependent on morphology (as stilbenes), or even be useful in pharmacology (as trans-stilbene (TS) derivatives, namely trans-resveratrol (RSV) or trans-pterostilbene (PTB), exhibiting anticancer and antifungal activities). Surprisingly, despite the broad interest in the topic, experimental spectroscopic characterization of such complexes is still rare to date. Herein we aim to shed light on this issue. We analyse vdW complexes of hBN with different organic compounds: TS, RSV, PTB, and tetraphenylporphyrin (TPP). Firstly, all these compounds have different electric dipole moments ranging from 2.4 D for PTB down to 0 D for TS as well as their different orientations relative to molecular skeletons. Hence, the magnitude of vdW interaction and its spectroscopic manifestation would be different. We utilized different experimental spectroscopic (THz, Raman, FTIR, UV/Vis absorption, and fluorescence spectroscopy) and theoretical (DFT calculations with empirical dispersion correction to take vdW interaction into account) methods. The Raman spectra showed that vibrations localized on the functional groups with excess positive charge were blue-shifted, while those with negative charge exhibited red shifts in the spectra of a complex compared to the spectra of pure compounds. These trends were also confirmed by DFT calculations. The THz absorption spectra of the vdW complexes demonstrated the presence of additional weak bands that can be assigned to the librations of molecules relative to the hBN surface. For weakly bonded TS + hBN complex fluorescence exhibited the relative enhancement of the TS vibronic line and slightly faster fluorescence decay. For polar TPP, notable red shifts were observed in both absorption and fluorescence spectra of the complex compared to pure TPP.

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