Spectroscopic Study of Proflavine Adsorption on the Carbon Nanotube Surface

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Despite the fact that non-covalent interactions between various aromatic compounds and carbon nanotubes are being extensively investigated now, there is still a lack of understanding about the nature of such interactions. The present paper sheds light on one of the possible mechanisms of interaction between the typical aromatic dye proflavine and the carbon nanotube surface, namely, π-stacking between aromatic rings of these compounds. To investigate such a complexation, a qualitative analysis was performed by means of ultraviolet visible, infrared, and nuclear magnetic resonance spectroscopy. The data obtained suggest that π-stacking brings the major contribution to the stabilization of the complex between proflavine and the carbon nanotube.

Index Headings: **Carbon nanotube; Complexation; π-Stacking; Proflavine; Spectroscopy.**

INTRODUCTION

Recently, new fields of science related to the investigation of non-covalent interactions between carbon nanotubes (CNTs) and both small molecules (ligands)[1] and polymers (such as DNA)[1–3] were extensively developed. The interest to this problem is due to the discovery of new physico-chemical and biophysical CNT applications. In particular, intermolecular interactions between aromatic compounds and the CNT surface provide the possibility of their solubilization.[4,5] From medico-biological viewpoint, one of the very promising directions is the use of CNTs as a carrier of drugs adsorbed onto its surface into cell.[6,7] This mechanism can also be effectively used in chemotherapy since CNTs can act as interceptors of biologically active aromatic compounds. The interceptor properties of aromatic compounds have been studied quite well to date in molecular biophysics[8,9] and can be used for manipulation of the active drugs' concentrations as well as their biological effects.[10,11] In particular, it has been suggested that the complexation between CNTs and an antitumor antibiotic can regulate the medico-biological activity of the drug.[7] This stimulated a number of studies on the interaction between antibiotics,[7,12,13] dyes,[14–16] and other compounds[17–20] and the CNT surface. For instance, the two-component systems of CNTs and phenothiazine dyes (methylene blue[21–23] and thionine[24,25]) have been investigated in much detail. However, there is still a lack of general understanding of the nature of the interaction between the ligands and CNTs.

This paper is devoted to the spectroscopic study of the interaction between the aromatic acridine mutagen proflavine (PF) and CNTs. This molecule has been chosen for the study because it contains a planar chromophore that should presumably contribute to the formation of a complex stabilized by the overlapping π-electron systems of the PF chromophore and the fragments of CNT surface.[26] In addition, for a long time PF has been used in molecular biophysics as a model of a typical DNA-binding compound.

MATERIALS AND METHODS

Preparation of the Stock Solution of Proflavine. Within the framework of the present investigation, two stock solutions of PF hydrochloride (Fig. 1) were prepared by solubilization of accurately weighed dry material (Sigma Aldrich, Cat. No.: P-4646). All weightings were performed by means of an analytical microbalance, ANG-50C (Axis, Poland). For the purposes of infrared (IR) and nuclear magnetic resonance (NMR) studies, 3.8 mg of PF were dissolved in 5.155 mL of heavy water (D_2O; Sigma Aldrich, Cat. No.: 151 882), resulting in a solution with concentration 3 mM.

The stock solution of PF in water (H_2O) was prepared using the following protocol. The stock solution of PF with concentration 0.25 mM was prepared by dissolving 1.7 mg of dry material in 27.675 mL of double-distilled H_2O. The solution with concentration 0.025 mM was obtained by transferring 0.2 mL of the stock solution to quartz cuvette 1 and then adding 1.8 mL of double-distilled H_2O. After that, 1 mL of this solution was transferred from quartz cuvette 1 to quartz cuvette 2. Finally, 1 mL of double-distilled H_2O was added to cuvette 1 and the same volume of the CNT solution was added to cuvette 2. Thus, in cuvettes 1 and 2 the solutions of pure PF and PF-CNT, respectively, were obtained with a PF concentration 0.0125 mM.

Preparation of the Carbon Nanotube Solution. Single-wall closed CNTs were kindly given to us by E. D. Obraztsova (Moscow, Russia). Their diameters were distributed over the range 1.0–1.6 nm with a maximum fraction of 1.4–1.5 nm.[2] The solutions of CNTs were prepared in doubly-distilled H_2O as follows. The solution was prepared by placing 1 mg of dry CNTs with double-distilled H_2O into a 1.5 mL plastic test tube (Eppendorf, Germany). The test tube was sealed using film (Parafilm,

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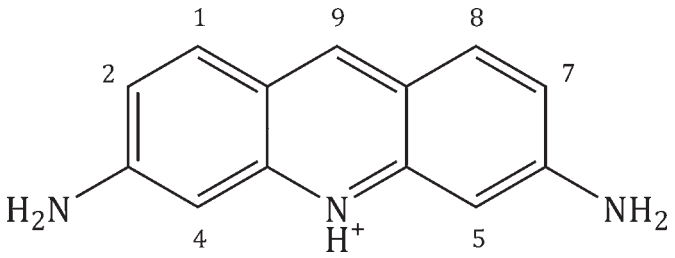

FIG. 1 Structure of the PF molecule; numbers designate the non-exchangeable protons.

USA) and was placed into the H_2O-filled waveguide of an ultrasonic homogenizer (UZDN-A, Ukraine). The homogenization of the CNT solution was carried out for 20 min. By the end of this procedure, sedimentation of the remaining solid phase was performed by centrifugation (5000 rotations per min) for 15 min. After centrifugation, the supernatant containing the suspended fine was removed from the test tube and placed into another test tube, which was treated in the same way. The described procedure was repeated at least three times until a clear CNT solution was obtained.

CNT solutions for the IR and NMR experiments were prepared in a similar way, with the only exception being that, instead of doubly distilled H_2O, the CNTs were solubilized directly in a PF-D_2O solution with concentration 3 mM.[4]

Measurements. For the ultraviolet visible (UV-Vis) experiment, the absorption spectra were recorded by means of a double-beam spectrophotometer SQ-4802 (UNICO, USA) in the range of 230–900 nm with a 0.5 nm step. The processing of the spectra was made using UV-Vis Analyst software (version 4.67).

For the NMR experiment, 400 MHz ^{1}H NMR spectra were recorded on an Avance NMR spectrometer (Bruker, Germany). Chemical shifts of non-exchangeable protons were measured relative to an internal reference, tetramethylammonium bromide (TMA), and recalculated with respect to sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS): $\delta_{DSS} = \delta_{TMA} + 3.178$ parts per million (ppm). Measurements were made using standard 5 mm NMR tubes containing a minimum volume of 0.5 mL of solution at $T = 298$ K. All NMR measurements were made in the fast-exchange condition for the interacting molecules on the NMR time scale. The assignment of PF protons was made according to the previously published data.[27]

For the Fourier transform infrared (FT-IR) experiment, an IFS-66 instrument (Bruker, Germany) with a reflection attachment (angle of incident beam of 16.5°) was used to record the FT-IR spectra of PF and its complexes with single-wall carbon nanotubes (SWCNTs) in the reflectance mode in the range 400–4000 cm^{-1}. Evaluation and processing of the spectra were performed using Opus software (version 5.5). The accuracies of determination of the wavenumbers and transmittance were 0.01 cm^{-1} and 0.1%, respectively.

Molecular Modeling. The procedure used for molecular modeling of the PF-CNT complex corresponds in general to those used previously for studying of different complexes of aromatic molecules in aqueous solutions.[28] Briefly, the method of structure calculations is based on the following protocol. The calculation of the spatial

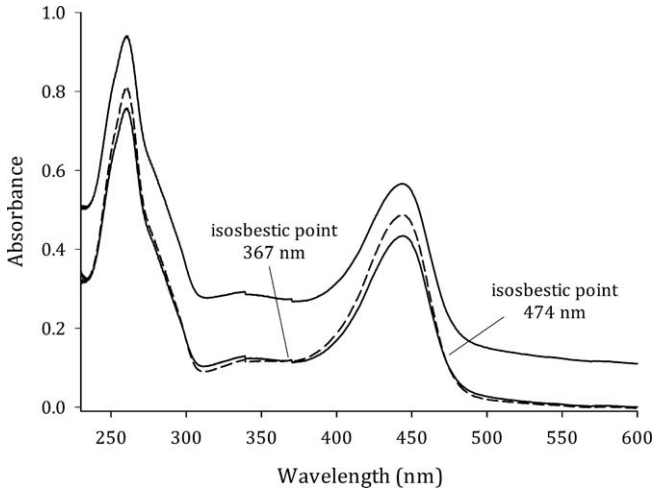

FIG. 2. The UV-Vis spectra of the PF solution (dashed line), PF-CNT solution measured with respect to H_2O (upper solid line), and PF-CNT solution measured with respect to pure CNT solution (lower solid line); PF concentration is 0.0125 mM.

structures of a 1:1 PF-CNT complex was performed using the methods of molecular mechanics and X-PLOR software (version 3.851)[29] with the CHARMM27 force field. Modeling of the aqueous environment of the interacting molecules was performed using H_2O molecules in the form TIP3P, placed in a cubic box with side length 35 Å (1423 molecules). The topology of all molecules and parameterization of their valent interactions were obtained using XPLO2D software.[30] Quantum mechanical calculations of partial atomic charges on CNT and PF atoms were performed using Gaussian 03 software[31] within the framework of DFT (B3LYP) in 6-31G* basis set using the Merz–Kollman method.

RESULTS AND DISCUSSION

Figure 2 shows the absorption spectra of the solutions of pure PF (dashed curve), PF-CNT measured with respect to H_2O (upper solid curve), and PF-CNT measured with respect to the pure CNT solution (lower solid curve). The region of 600–900 nm is not presented because of the absence of any specific spectral changes in this range. The systematic increase in absorption reflects the contribution of light scattering from the CNTs. In this regard, for this analysis the most interesting spectra are the two lower spectra because they explicitly demonstrate spectral changes on the addition of CNTs to the PF solution without the contribution of light scattering from the CNTs. There is a bathochromic shift of the absorption band of PF (the absorption maximum of pure PF at wavelength 443.5 nm has shifted for 1 nm in the mixture with CNTs to 444.5 nm). A hypochromic shift of the absorption band of PF is also clearly observed, with the magnitude of hypochromism amounting to 11%. In addition, the spectra show two isosbestic points at 367 nm and 474 nm. Similar changes of the visible spectra were also observed previously for the binding of phenothiazine derivatives with CNT[22,25] and of various aromatic compounds with C_{60} fullerene.[32] All these factors, together with the data from the literature,[6,16–18,20,23,33–37] indicate that the complexation

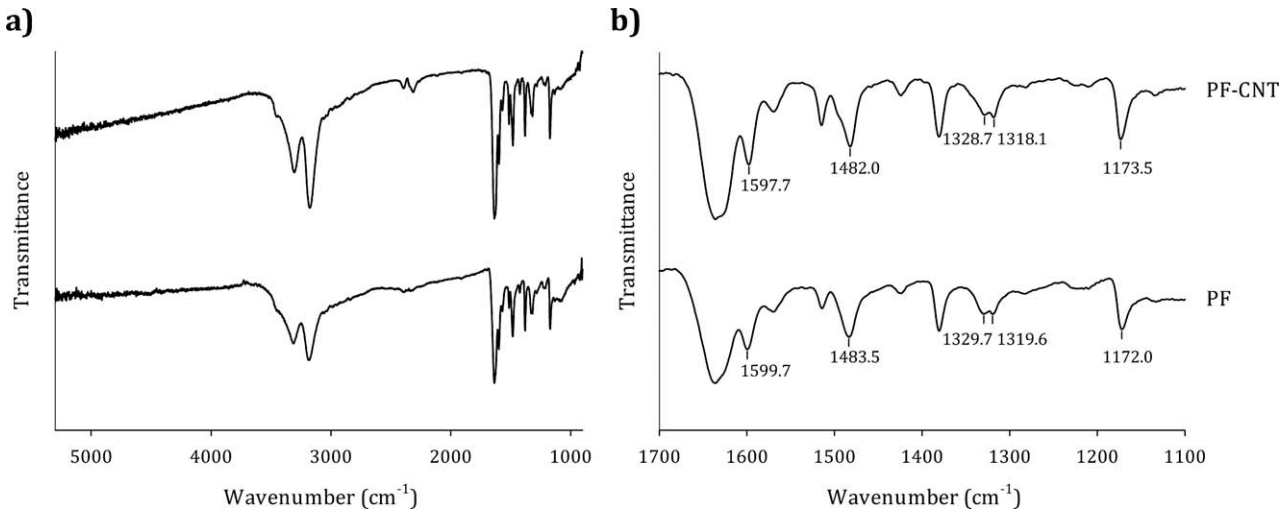

FIG. 3. The IR spectra of the pure PF and PF-CNT solutions; PF concentration is 3 mM. The left panel (**a**) shows the spectra in the whole region, whereas the right panel (**b**) demonstrates those parts of spectra which contain only characteristic bands of proflavine.

between PF molecules and the CNT surface in solution is probably stabilized by π-stacking.

Figure 3 shows the IR spectra of the PF and PF-CNT solutions. The characteristic slope of the spectrum baseline registered in the whole spectral range is caused by Rayleigh light scattering from the CNT surface (Fig. 3a). The assignment of PF peaks was accomplished according to previously published data,[38] grounded in quantum chemical computation of the IR spectrum of acridine orange,[39] which is a close analog of PF. Proflavine exhibits characteristic absorption peaks at 1633, 1598, 1514, and 1319 cm^{-1} (the C=C stretching mode); at 1624, 1568, and 1483 cm^{-1} (the C–N stretching mode); at 1173 and 1130 cm^{-1} (the C–H bending mode); and at 1424, 1380, and 1329 cm^{-1} (the N–H bending mode). Some bands of the IR spectrum corresponding to the vibrations of atomic groups of the PF molecule (see Fig. 3b) shifted slightly on the addition of CNTs (see Table I). The magnitude of the low-frequency shift (about 2 cm^{-1}) observed for the 1598, 1319 (the C=C stretching mode), and 1483 (the C–N stretching mode) cm^{-1} bands of PF is in accord with the governing role of π-stacking in the reaction of non-covalent complexation. It should be noted, however, that the measured shifts are relatively small compared to typical IR shifts of about 2–10 cm^{-1} observed on the complexation of aromatic compounds in aqueous solution in the millimolar concentration range.[40] This fact may be interpreted in terms of a compensation effect caused by the disruption of PF aggregates on the addition of CNTs to the solution; that is, the high-frequency shift (disruption of the aggregates) is overbalanced by the low-frequency shift (complexation with the CNT surface), which results in a relatively small net shift of the vibrational frequency of the atomic groups.

TABLE I. Experimental vibrational frequencies (in cm^{-1}) of the PF molecule in a free state and bound with CNT.[a]

PF	PF-CNT	Vibration
1636.3	1635.8	C=C stretching mode
1599.7	1597.7	C=C stretching mode
1514.3	1514.8	C=C stretching mode
1483.5	1482.0	C=N stretching mode
1329.7	1328.7	N–H bending mode
1319.6	1318.1	C=C stretching mode
1172.0	1173.5	C–H bending mode

[a] See Fig. 3b.

Figure 4 shows the ^{1}H NMR spectra of the samples studied. An important specific property of these spectra is the absence of the broadening of spectral lines of the mixture compared to those of the pure PF solution. The average low-frequency shift of about $\Delta\delta = 0.02$ ppm is clearly observed for the signals corresponding to aromatic PF protons. The values of the chemical shifts for the aromatic protons in the PF and PF-CNT solutions are shown in Table II. The low-frequency shift indicates the shielding effect ($\Delta\delta > 0$), which can be caused by the magnetic field of the π-conjugated system of aromatic rings constituting the surface of the CNT. The increased shielding (by approximately 0.02 ppm) of the central PF protons, H9 and H4/5, compared to the peripheral protons, H1/8 and H2/7, suggests that the PF molecule is predominantly oriented perpendicular to the longitu-

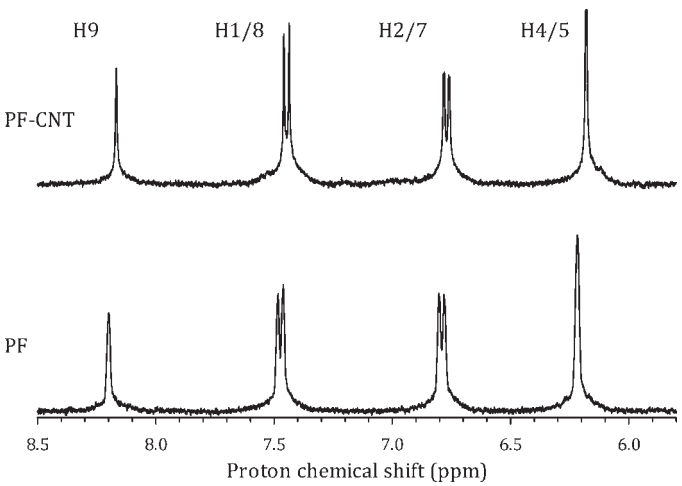

FIG. 4. The ^{1}H NMR spectra of the pure PF and PF-CNT solutions; PF concentration is 3 mM.

TABLE II. Values of chemical shifts (in ppm) of non-exchangeable PF protons in a free state and bound with CNT.[a]

	H9	H1/H8	H2/H7	H4/H5
PF	8.20	7.47	6.79	6.22
PF-CNT	8.17	7.45	6.77	6.18
Difference	0.03	0.02	0.02	0.04

[a] See Fig. 1.

dinal axis of the CNTs, when the peripheral protons are located slightly away from the CNT surface. The corresponding energy-minimized structure of the PF-CNT complex is shown in Fig. 5. Such a perpendicular structure is hydrophilically favorable, allowing the interaction of the PF amino groups with the aqueous environment.

To verify that the measured values of the magnetic shielding are meaningful and originate from the magnetic shielding in π-stacked complex, we calculated the magnitudes of $\Delta\delta$ according to the method of magnetic dipole in vacuo,[41] which accounts for the ring-current effect's playing a dominant role in stacking between the aromatic molecules in aqueous solution.[42] Within the framework of this method, it is assumed that the magnetic dipole with a dipole moment $\mu_i = 6$ is placed in the center of each *i*th hexagonal carbon cycle of the CNT surface. The net shielding can be calculated by taking the summation of $\Delta\delta_i$, created by each dipole at a given point with radius vector $\mathbf{r}_i$ and located at a distance 0.34 nm away from the CNT surface (typical of the complexes of aromatic molecules[40]):

$$\Delta\delta = \sum_i \frac{\mu_i(1 - 3\cos^2\Theta_i)}{\mathbf{r}_i^3},$$

where the angle Θ_i is measured with respect to the axis of the dipole μ_i.

Figure 6 shows the typical dependence of $\Delta\delta$ on the distance along the nanotube axis for PF placed 0.34 nm away from the CNT surface having the mean diameter of

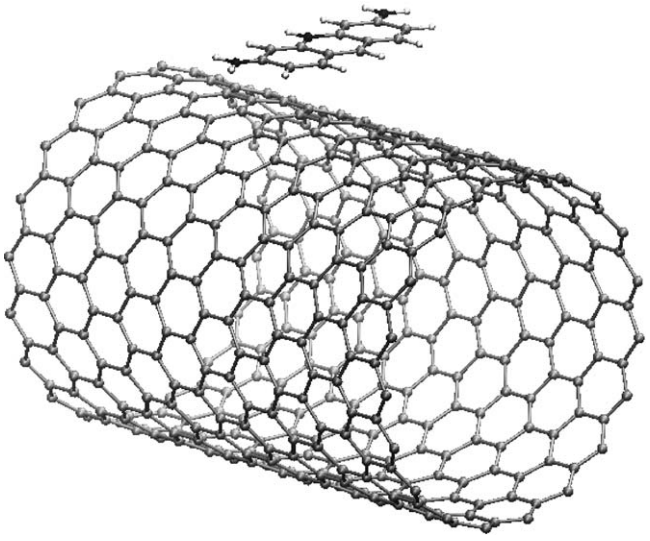

FIG. 5. Energy-minimized structure of the PF-CNT complex.

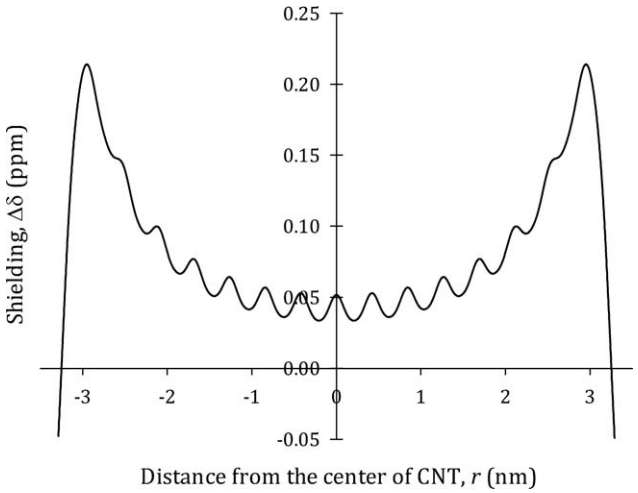

FIG. 6. Dependence of the calculated shielding of the H9 proton of PF molecule on the magnitude of the shift of the ligand along the CNT surface (for the other protons, this dependence is the same).

1.47 nm. Along the nanotube axis, the magnitude of $\Delta\delta$ is determined as a superposition of the positive and negative contributions from the shielding cone of the carbon rings located both to the right and to the left of the ligand. Moving the ligand to the edges of the CNT results in an increase in the shielding as a consequence of the absence of the de-shielding contribution from one of the halves of the CNT. If the edge effects are neglected under the extreme limit of infinitely long CNT, we can get an estimated magnitude of the shielding along the nanotube axis equal to 0.05 ppm, which agrees well with the $\Delta\delta$ values given in Table II. It should be noted that this method of estimating the shielding is very approximate; it does not allow us to distinguish the parallel and perpendicular orientations of the ligand on the CNT surface or to give an interpretation to the difference in the shielding of different PF protons in Table II. Most likely the observed difference in the shielding of the PF protons is also caused by local shielding effects from the water molecules in the PF-CNT complex.

CONCLUSION

The data obtained using three different spectroscopic techniques (UV-Vis, IR, and NMR) suggest the formation of stable complexes between PF molecules and CNTs in aqueous solution. Qualitative analysis has shown that the most probable mechanism of PF-CNT complex stabilization is π-stacking of electronic systems of PF chromophores and CNT surfaces, which agrees well with recently published data on CNTs as well as ligand binding with fullerenes. In particular, we found that PF may adopt a perpendicular orientation with respect to the longitudinal axis of the CNT, maintaining an energetically favorable hydrophilic contact with H_2O molecules. The complexation is accompanied by low-frequency shifts in both the IR and NMR spectra, as well as a bathochromic shift of the absorption maximum in UV-Vis spectra. Taken as a whole, the results of the present work deepen our understanding of the mecha-

nism of the stabilization of aromatic drug–CNT complexes in aqueous solution.

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