Spectroscopic changes induced by sonication of porphyrin-carbon nanotube composites in chlorinated solvents

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Abstract

We report the spectroscopic changes of tetraphenylporphyrin carbon nanotube composites in a variety of chlorinated solvents such as chloroform, dichloroethane and dichlorobenzene as a result of sonication. Detailed data analysis suggests that protonation of the porphyrin core nitrogen atoms occurs as a result of sonodegradation of the solvent molecules. Extreme care must be taken when working with carbon nanotube composite solutions in chlorinated solvents, as sonication is always employed to disperse the nanotubes. When working with molecules that are capable of acting as a base some

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amount of protonation is inevitable and this may dramatically change the physicochemical properties of the composite materials.

1. Introduction

Functionalization of nanotubes is extremely important as it couples the mechanical and structural strength of the carbon skeleton with desirable optical properties imparted by the molecules that are used to decorate the carbon exo-surface.

Porphyrins represent one such family of functional molecules with potential applications as sensitizers for photoactive switches, light-harvesting systems, in cancer photodynamic therapy and electronics. [1-6] Porphyrins are also particularly important as suitable partners of carbon nanotubes in composites [7-14] due to their (electro) luminescence and photovoltaic properties as well as to their biocompatibility. Regardless of the functional molecule, sonication is a key step in the dispersion of single-walled carbon nanotubes (SWCNT) when making composite solutions, and chloroform is frequently the solvent of choice. [15,16] However, sonication of a variety of halogenated solvents [17-20] may produce degradation products that can react with moieties on the composite thus hampering and complicating both characterization and function of the resulting material. In the study reported herein, we employ absorption, emission and ^{1}H-NMR spectroscopy to investigate the effect of sonication and protonation on the optical properties of tetraphenylporphyin and zinc tetraphenylporphyrin solutions in different solvents before and after the addition of SWCNT.

We demonstrate that spectroscopic changes of porphyrins in composite solutions are due to protonation of the porphyrin resulting from sonolysis of a variety of chlorinated solvents and neither to interaction with the nanotubes nor to decomposition of the porphyrin macrocycles as previously reported by others.

2. Experimental Section

2.1 Materials

Purified single walled nanotubes were produced by the HiPCO method, purchased from Carbon nanotechnologies Inc and used as supplied (lot #PO289). Chemicals were purchased from commercial sources and were used as received. The polymer PPyPV was prepared modifying a literature procedure. [21] Molecular weight and polydispersity (PDI) of PPyPV (Mw=24,421; PDI=2.8) were determined by GPC on a Waters 600E pump with a Waters 486 tunable absorbance detector @ 260 nm. The THF polymer solution was injected at a flow rate of 1 mL/min, against polystyrene standards. Solutions were filtered through a Millipore membrane with a porosity of 0.45 mm just before injection. The number-average degree of polymerization was estimated to be approx. 20 from the number-average molecular weight (Mn) and the molecular weight of the repeating unit (462). Chloroform was purified on a column of basic alumina (grade I, 10g/14ml) in order to remove all impurities, including the residual traces of HCl always present in this commercially available organic solvent.

2.2 Preparation of composites

HiPCO SWCNTs were added to solutions of the porphyrins in different solvents such that the porphyrin : SWCNT mass ratio was 1 : 1. Sonication was performed for different times using a high power ultrasonic tip (model GEX600, 120W, 60kHz) and a low power sonic bath (Ney Ultrasonik).

Characterization: Absorption spectra were recorded with a Shimadzu UV3100 UV-Vis-NIR spectrometer. Emission spectra were recorded with a Perkin-Elmer LS-55 luminescence spectrometer, with an excitation wavelength equal to the Soret band of the porphyrin in each case using quartz cells (path length = 10 mm). Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded with a Bruker DPX 600 at 25°C, using the deuterated solvent as lock using quartz tubes (diameter = 5 mm).

3. Results and Discussion

3.1. Absorption Spectroscopy

The absorption spectrum of an unsonicated red solution of tetraphenylporphyin TPP (Figure 1a) in chloroform shows a typical Soret band at 418 nm and four Q-bands at 516, 550, 590 and 646 nm. Addition of SWCNTs to form the TPP : SWCNT composite causes a color change from red to green. The absorption spectrum of the composite solution looks very different, with a Soret band shifted at 446 nm and two Q-bands at 610 and 660 nm (Figure 1d).

Baskaran et al. previously reported similar changes for a TPP derivative in chloroform (5-p-hydroxyphenyl-10,15,20- tritolylporphyrin); the changes were attributed to the

interactions between residual acid groups on the surface of the carbon nanotubes and the grafted porphyrin molecules. [22] We indeed observe a red shift when chloroform is used as a solvent for TPP : SWCNT composites, but we postulate that this change may, in fact, be the result of protonation of the porphyrin molecules upon sonication in chloroform.
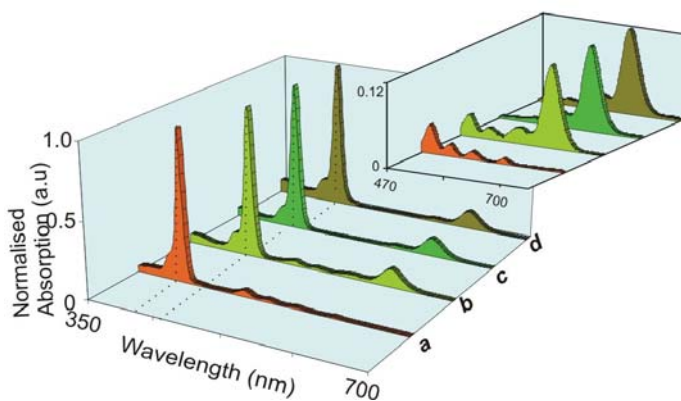

Figure 1: Absorption spectra of a solution of TPP (a) before sonication, (b) after tip sonication for 2 minutes (c) after addition of 150 equivalents of HCl and of (d) a composite solution of TPP : SWCNTs sonicated for 1 minute (4.5 µM, CHCl3, 25°C). Inset: partial absorption spectra magnified to show the variations of the Q-bands

Sonication is a key step in the dispersion of single-walled carbon nanotubes (SWCNT) when making composite solutions. We therefore investigated the effect of sonication of a solution of TPP in chloroform. The absorption spectrum of the sonicated solution shows a Soret band at 446 nm and the color of the solution changes from red to green. Also the

characteristic porphyrin Q-bands are converted to two bands at 610 and 660 nm (Figure 1b). The red shifted Soret band and the pattern of Q- bands in those sonicated solutions suggest that the porphyrin molecules exist in a protonated form. We propose that hydrochloric acid created by sonodegradation of chloroform [23,24] causes the protonation of the core nitrogen atoms of the porphyrins. To confirm this hypothesis we added hydrochloric acid to unsonicated porphyrin solution. Upon protonation, the absorption spectrum (Figure 1c) looks identical to the one for the sonicated TPP and TPP : SWCNT composite solutions, with a Soret band at 446 nm and two Q bands at 610 and 661 nm.

The equilibrium nature of the protonation mechanism was confirmed by the observation of an isosbestic point at 429 nm during the titration in chloroform (Figure 2). Addition of a few drops of triethylamine shifted the Soret band back to 418 nm. To support our hypothesis we added trifluoroacetic acid (TFA) to unsonicated TPP solutions. The absorption spectrum of TPP protonated with TFA showed a 22 nm red shift of the Soret absorption band to 440 nm, and a similar bathochromic shift of the Q bands to 604 nm and 654 nm (Figure 3). Yu et al. reported that the effect of the acid counterion significantly affects the Stokes' shift observed upon protonation, with the chloride ion showing the largest red shift of all the acids studied. [25] This is fully consistent with our findings above, with a red shift of 28 nm observed for the TPP solutions protonated with HCl, and a shift of 22 nm observed for the ones protonated with TFA. These results confirm that HCl must be the acid responsible for the TPP protonation upon sonication,

as a Soret peak at 446 nm and Q band peaks at 610 and 661 nm are characteristic of TPP

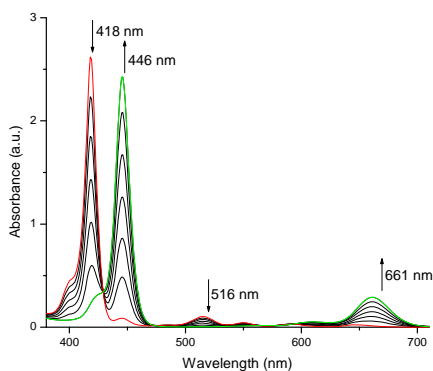bi-protonated with HCl in chloroform, due to the involvement of the acid counterion.

Figure 2: Absorption changes of TPP (4.5 µM, CHCl$_3$, 25°C) upon addition of increasing

amounts of HCl (0, 25, 50, 75, 100, 125, 150 equivalents). The spectral changes represent

protonation equilibrium between two forms of porphyrin.

The same sonication-induced protonation behavior was also observed for Zn-TPP

solutions. However, a far greater amount of energy was required for protonation of the

metalloporphyrins to take place, which is which is consistent with the fact that each

nitrogen atom is already engaged in a coordinate-covalent bond with the central metal

ion. After addition of HCl the Soret band shifted at 437 nm and two Q-bands at 551 and

652 nm appeared (Figure 4). Addition of a few drops of triethylamine yielded an

absorption spectrum identical to that of the free base TPP, with the Soret band at 418 nm,

indicating that the zinc cation is not reintroduced into the cavity of the porphyrin macrocycle.
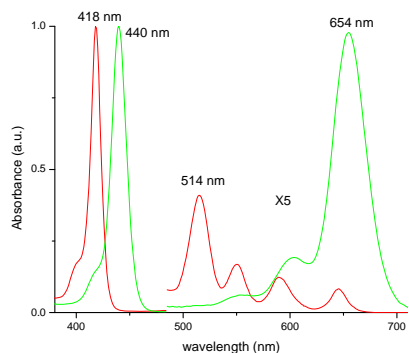

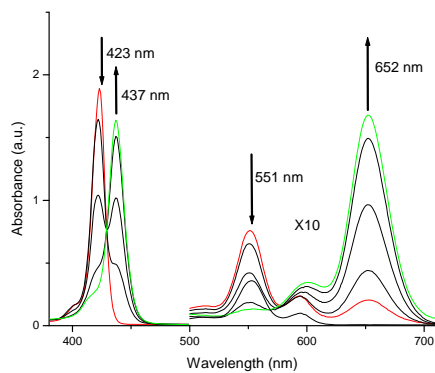Figure 3: Absorption changes of TPP (4.5 µM, CHCl$_3$, 25°C) upon addition of TFA.

Figure 4: Absorption changes of Zn-TPP (4.5 µM, CHCl$_3$, 25°C) upon addition of increasing amounts of HCl.

Yen et al. reported the decomposition and demetalation of porphyrins by ultrasonication. [26] They report that the decomposition is most efficient in chloroform, although water is a co-solvent and the decomposition is ascribed to the generation of oxidizing species rather than to HCl. In order to confirm that the spectroscopic changes observed were actually due to protonation of the porphyrins and not to decomposition, we studied the effect of sonication of a pH indicator, azopyridine (AZ) in chloroform and other solvents. The absorption spectrum of an orange solution of AZ in chloroform (Figure 5a) shows a strong band at 428 nm. After one-minute tip sonication the absorption band at 428 nm disappears and a new band at 540 nm appears (Figure 5b), and the solution turns red-purple. Identical changes were found for the protonated AZH form [27] confirming that AZ is completely protonated upon sonication in chloroform.
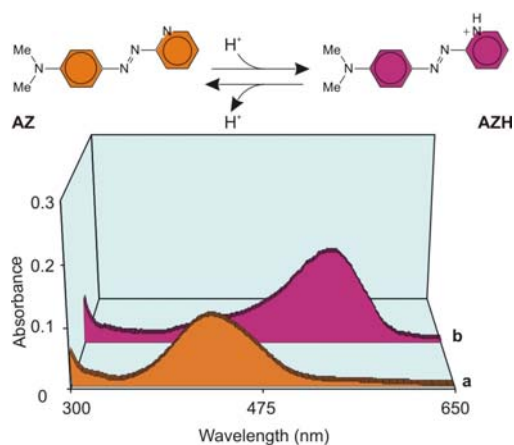

Figure 5: Absorption spectra of AZ in CHCl$_3$ (a) before and (b) after tip sonication for 1 minute.

3.2. Emission Spectroscopy

The fluorescence properties of the sonicated and unsonicated porphyrin and composite solutions were also investigated. Excitation at the Soret band of a chloroform solution of TPP results in two emission peaks at 650 and 715 nm, typical for such porphyrin molecules (Figure 6a). The emission spectrum of the sonicated TPP : SWCNT composite solution is very different, showing a broad emission band with the maximum located at 685 nm (Figure 6d). After sonication (Figure 6b) and after addition of acid (Figure 6c), the emission observed was indistinguishable from that of the sonicated composite solution.
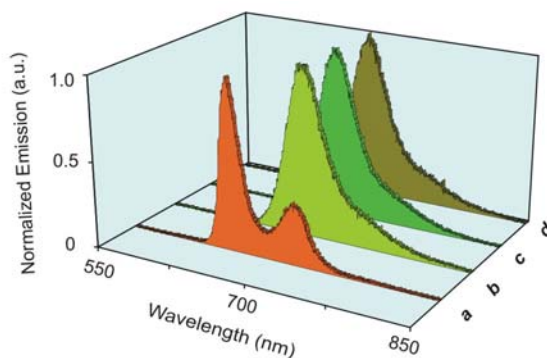

Figure 6: Emission spectra of a solution of TPP (a) before sonication, (b) after sonication for 2 minutes (c) after addition of 150 equivalents of HCl and of (d) a composite solution of TPP : SWCNTs. Excitation at the corresponding Soret band in all cases (6.5 μM, CHCl₃, 25°C).

Emission spectra for solutions of the Zn-TPP molecule with and without SWCNT displayed a similar red shift of 45 nm of the peak emission band from 603 nm to 648 nm upon sonication.

3.3. Proton Nuclear Magnetic Resonance Spectroscopy

The ^{1}H-NMR spectrum of a CDCl$_3$ solution of TPP (TPPH$_2$ Figure 7a) shows a singlet at 8.9 ppm for the β-pyrrole protons H^1, a doublet at 8.2 ppm for the ortho-phenyl protons H^2 and a multiplet at 7.8 ppm corresponding to the overlapping signals for the meta-phenyl and the para-phenyl protons H^3 and H^4. The addition of acid alters significantly the chemical shifts of all the aromatic protons (Figure 7c). The largest change is observed for the doublet of the ortho-phenyl protons, which shifts by ca. +0.4 ppm after the addition of ten equivalents of CF$_3$CO$_2$H (H^6). The metha and para-phenyl protons move downfield and broaden significantly (H^7, H^8). The signal of the β-pyrrole protons moves upfield upon protonation (H^5). After two minutes sonication the ^{1}H-NMR spectrum contains superimposed signals of both TPPH$_2$ and TPPH$_4{}^{2+}$ at their normal chemical shift values (Figure 7b). The ^{1}H-NMR spectrum of a CDCl$_3$ solution of the composite (Figure 7d) contains signals of both TPPH$_2$ and TPPH$_4{}^{2+}$. The signals are broadened, probably due to interactions of the porphyrin with the carbon nanotubes.
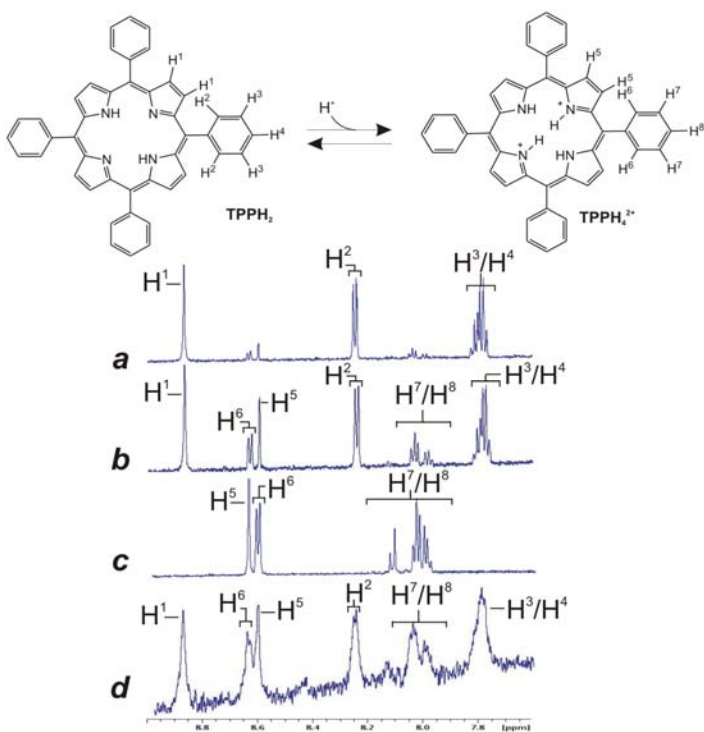
Figure 7: Partial ^{1}H-NMR spectra of a solution of TPP (a) before sonication, (b) after sonication for 2 minute (c) after addition of 10 equivalents of TFA and (d) of a composite solution of TPP : SWCNTs (4.5 mM, CDCl$_3$, 25°C, 600 KHz).

3.4. Other Solvents

We performed sonication experiments of TPP solutions in dichloroethane (DCE), dichlorobenzene (DCB) and dichloromethane (DCM) and other non halogenated solvents commonly used to disperse nanotubes such as N,N-dimethylformamide (DMF), N-methylpyrrolidone (NMP) and tetrahydrofurane (THF) in order to explore if sonication of other solvents will produce degradation products that can react with composites The same spectral shifts were observed upon sonication of TPP in dichloroethane and

dichlorobenzene and complete protonation was found after sonication for 2 minutes and 30 seconds respectively (See Figure S2 and S3 in the Supporting Information). Protonation did not take place for TPP in dichloromethane; the absorption spectrum of TPP remained unchanged after up to 90 minutes tip ultrasonication (See Figure S4 in the Supporting Information).
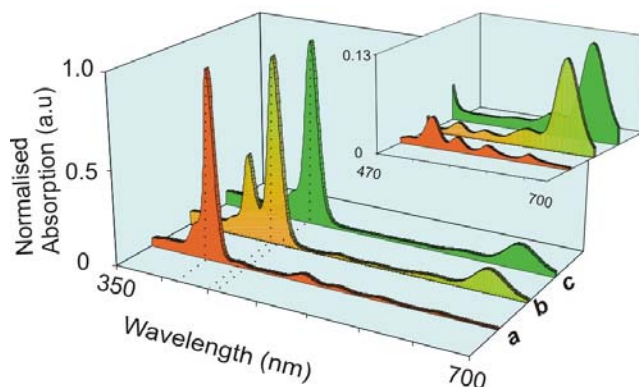

Figure 8: Absorption spectra of a solution of TPP after sonication for 1 minute in (a) DCM, (b) DCE (c) DCB (4.5 µmM, 25°C).

DCM was indeed found to have a much lower sonochemical degradation rate compared to the other chlorinated solvents. [17] No spectral shifts were observed when DMF, NMP and THF were used as solvents. After 1 minute tip sonication of a solution of TPP in DCM, DCE and DCB no protonation, partial and complete protonation was achieved respectively (Figure 8).

3.5. Sonication with Low-power Sonic Bath

We performed sonication experiments of TPP solutions in chloroform, DCE, DCB and DCM using a low power sonic bath.   We observed the same spectral shifts for TPP in dichloroethane and dichlorobenzene (Figure S5 and S6 in the Supporting Information), indicating that indeed HCl is produced even with mild sonication.   As already seen with the high-power sonic tip, protonation did not take place when dichloromethane was used as solvent; the absorption spectrum of TPP remained unchanged after up to 3 hours sonication in the bath (Figure S7 in the Supporting Information).

In order to find out how much acid is produced we performed titration studies of TPP and compared them with the sonication studies. The titrations of TPP in DCM showed an isosbestic point at 425 nm. (Figure 9).
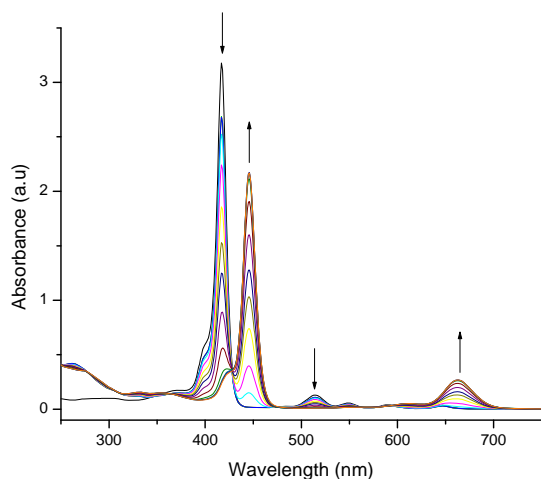

Figure 9: Absorption changes of TPP (4.5 µM, DCM, 25°C) upon addition of increasing amounts of HCl (0, 25, 35, 65, 85, 105, 125, 145, 165, 185, 205, 225, 245, 265 equivalents).

The titration results are presented by plotting the ratio of the relative intensity of the low-energy (red) absorption feature (i.e. Soret band of the free base porphyrin at 418 nm) to that of the high-energy (blue) absorption feature (i.e. Soret band of the porphyrin diacid at 446 nm) as a function of the equivalents of acid added (Figure 10). Such plots are commonly used, as they are extremely useful for illustrating titrations, accurately conveying the protonation progress and indicating saturation behavior where applicable. [15] Complete protonation of TPP was achieved after addition of 250 equivalents of acid,
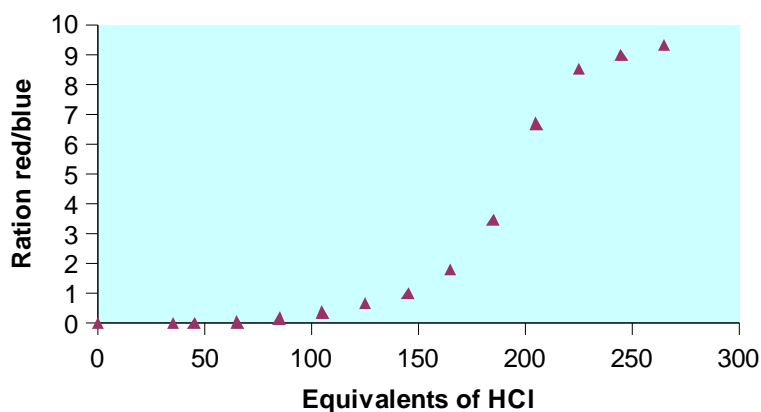
when the red to blue ratio reached a plateau of approx. 10.

Figure 10: Intensity ratio of the 446 nm protonated (red) absorption feature to the 418 nm (blue) feature of TPP (4.5 µM, DCM, 25°C).

The same red to blue ratio was found after mild sonication in chloroform and DCB for three minutes and ninety seconds respectively and a ratio of 4 was found after two hours of mild sonication in DCE.   These results indicate that indeed an enormous amount of

acid is generated with a short time of mild sonication of these chlorinated solvents. More than 200 equivalents of acid are generated after only a few minutes sonication of chloroform and DCB.

3.6. Effect of Nanotube on Protonation of Porphyrins

In order to check if the presence of nanotubes affects the extent to which the porphyrin molecules were protonated we performed titration studies of TPP with SWCNT and compared them with the previous ones without nanotubes. DCM was used as the solvent, as it was found to be stable upon sonication for prolonged periods of time. The titration of TPP : SWCNT in DCM showed an isosbestic point at 425 nm (Figure 11).
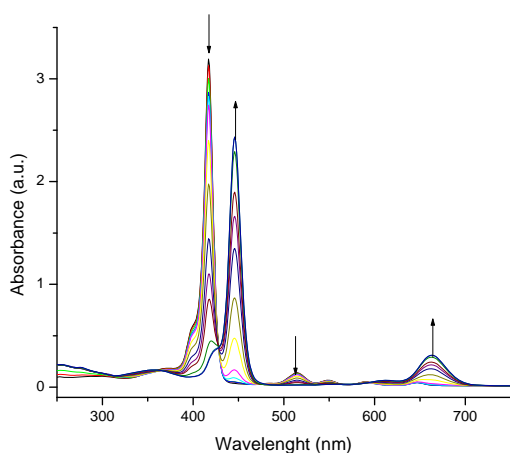

Figure 11: Absorption changes of TPP : SWCNT (4.5 µM, DCM, 25°C) upon addition of increasing amounts of HCl (0, 5, 15, 25, 35, 45, 65, 85, 105, 125, 145, 165, 185, 205 equivalents).

Complete protonation was achieved after addition of 185 equivalents of acid to the sonicated TPP : SWCNT composite solutions in DCM (Figure 12). The amount of HCl required to fully protonate TPP was reduced through the addition of SWCNTs. This indicates that the presence of SWCNT accelerates porphyrin protonation.
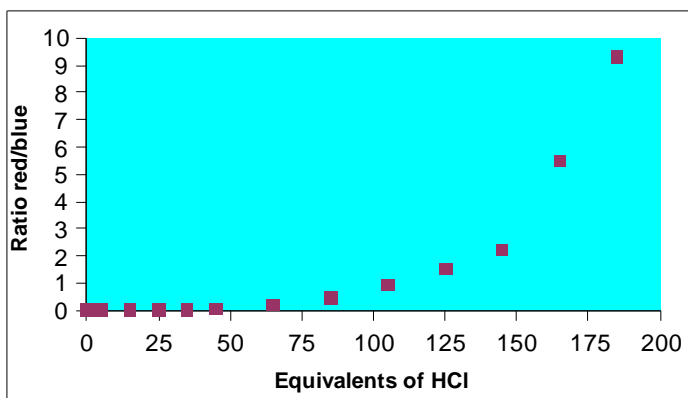

Figure 12: Intensity ratio of the 446 nm protonated (red) absorption feature to the 418 nm (blue) feature of TPP:SWCNT.

Steuerman et al. reported similar protonation behavior for the basic polymer poly(2,6-pyridinylenevinylene)-co-[(2,5-dioctyloxy-p-phenylene) vinylene] upon addition of carbon nanotubes. [15] The solvent used for their studies was chloroform. The absorption spectrum of a solution of PPyPV in chloroform (Figure 13a) shows a strong band at 418 nm. After two minutes tip sonication the absorption band at 418 nm disappears and a new band at 540 nm appears (Figure 13b). Identical changes were found for the protonated PPyPVH form confirming that the polymer is completely protonated

upon sonication in chloroform. Our experiments suggest that protonation is at least partially caused by sonication during composite preparation; neglecting the sonication effects may lead to erroneous or misleading interpretations of spectroscopic data.
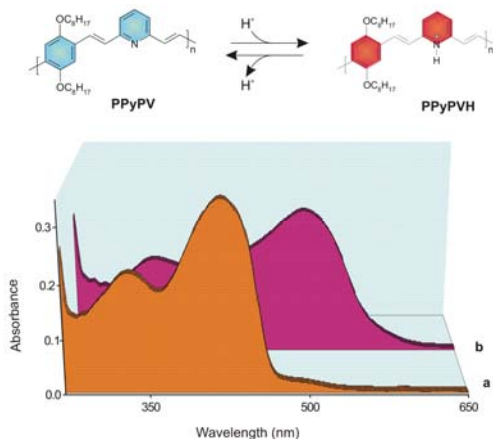

Figure 13: Absorption spectra of a solution of PPyPV (a) before sonication, (b) after tip sonication for 2 minutes.

4. Conclusions

In summary, tetraphenylporphyrin carbon nanotube composites were found to be protonated in chloroform, dichloroethane and dichlorobenzene upon sonication. The protonation took place using both a high power ultrasonic tip and a low power sonic bath. Absorption, emission and ^{1}H-NMR spectroscopy studies confirmed that the changes are consistent with HCl being generated during sonication. The results are compared to non-sonicated samples, ruling out the possibility that HCl is presenting the starting chloroform. Protonation of the porphyrin with TFA produced a shift in the absorption

spectra. Titration studies showed that more than 100 equivalents are needed to fully protonate the porphyrins. Only a few minutes of mild sonication of chloroform and DCB and a couple of hours of mild sonication of DCE fully protonate the porphyrin, which indicates that, indeed an enormous amount of acid is generated by sonication. Finally, the rate of porphryin protonation in DCM is increased by the presence of carbon nanotube. Therefore, extreme care must be taken when working with carbon nanotube composite solutions in halogenated solvents as protonation of acid sensitive molecules may take place during sonication, changing their physicochemical properties.

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List of Captions

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Figure 8: Absorption spectra of a solution of TPP after sonication for 1 minute in (a) DCM, (b) DCE (c) DCB (4.5 μmM, 25°C).

Figure 9: Absorption changes of TPP (4.5 μM, DCM, 25°C) upon addition of increasing amounts of HCl (0, 25, 35, 65, 85, 105, 125, 145, 165, 185, 205, 225, 245, 265 equivalents).

Figure 10: Intensity ratio of the 446 nm protonated (red) absorption feature to the 418 nm (blue) feature of TPP (4.5 μM, DCM, 25°C).

Figure 11: Absorption changes of TPP : SWCNT (4.5 μM, DCM, 25°C) upon addition of increasing amounts of HCl (0, 5, 15, 25, 35, 45, 65, 85, 105, 125, 145, 165, 185, 205 equivalents).

Figure 12: Intensity ratio of the 446 nm protonated (red) absorption feature to the 418 nm (blue) feature of TPP:SWCNT.

Figure 13: Absorption spectra of a solution of PPyPV (a) before sonication, (b) after tip sonication for 2 minutes.