

COVALENT LINKING OF Ni (II) COMPLEX OF MESO TETRA(4-AMINOPHENYL) PORPHYRIN WITH SINGLE-WALLED CARBON NANOTUBE AND ITS PHOTO-PHYSICAL PROPERTIES

D. R. Anakha and R. Yamuna✉

Center of Excellence in Advanced Materials and Green Technologies (CoE-AMGT), Dept. of Sciences, Amrita School of Engineering, Coimbatore-641112, Amrita Vishwa Vidyapeetham, (Tamil Nadu) India.

✉Corresponding Author: r_yamuna@cb.amrita.edu

ABSTRACT

5, 10, 15, 20 meso tetra(4-aminophenyl) porphyrinato nickel (II) complex (Ni-TAP) was connected covalently with a single-walled carbon nanotube (SWCNT). The Infrared (IR) spectrum of SWCNT-NiTAP nanohybrid conveys the shifting of C=O stretching frequency from 1714 cm^{-1} to 1695 cm^{-1} which substantiates the covalent bond connection of porphyrin with SWCNT. In Raman spectroscopy, there is a decrease in the I_D/I_G ratio after the covalent linkage of SWCNT with Ni-TAP compared to SWCNT-COOH, which specifies enriched electronic properties of SWCNT-NiTAP. This is perhaps due to the method of acylation. The morphology study of SWCNT-NiTAP retains the tube-like structure even after the covalent functionalization. The presence of significant peaks in the C 1s and N 1s XP spectra of SWCNT-NiTAP indicate the covalent bond connection of porphyrin chromophores on SWCNTs. Fluorescence spectra of SWCNT-NiTAP show that effective fluorescent quenching is due to energy or electron transfer from Ni-TAP to SWCNTs. Moreover, SWCNT-NiTAP reveals hypsochromic shift compared to Ni-TAP, which specifies the covalent linkage of SWCNT with Ni-TAP.

Keywords: Metalloporphyrin, Carbon Nanotube, Chromophore, Positive Solvatochromism, Hypso-chromic Shift, Nanohybrids.

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INTRODUCTION

Single-walled carbon nanotubes (SWCNTs) have more remarkable properties, mainly due to their strength, increased surface area per unit mass, electrical and thermal conductivity.¹⁻³ These properties can be additionally enriched through functionalization. The need for functionalization is prompted by the limited solubility of SWCNT in a common solvent. This functionalization was carried out by two methods, non-covalently and covalently. In covalent functionalization, a covalent bond has been formed between functional group entities of chromophores (porphyrin) and the carbon skeleton of SWCNT. Non-covalent functionalization has been done through a supramolecular complexation by the use of various adsorption forces and these forces include hydrogen bonding interactions, electrostatic force, Van der Waals force, π -stacking interactions, etc.⁴ Non-covalent functionalization of SWCNT exhibit better electronic properties as compared to covalent functionalization.² This is due to drastic oxidation condition and opening up of sidewall and further, there will be a change in hybridization from sp^2 to sp^3 during the direct covalent functionalization. This leads to a decrease in the conjugation of the SWCNT. However, the non-covalent functionalization of SWCNT loses the stability of the functionalized entity. Furthermore, the covalent functionalization of CNTs possesses better optoelectronic properties.⁵ Therefore, this is essential to functionalize the chromophore with SWCNTs without affecting the nano-tube structures. Functionalization of porphyrins with SWCNTs has been explored to construct photovoltaic devices.⁶⁻⁸

Porphyrins that are covalently connected can be examined as optical limiting devices, protective materials to the eyes, and optical devices against laser action.^{9-11,19} Porphyrins are chromophores that can absorb sunlight and further light energy is converted to electronic carriers. CNTs can carry this created

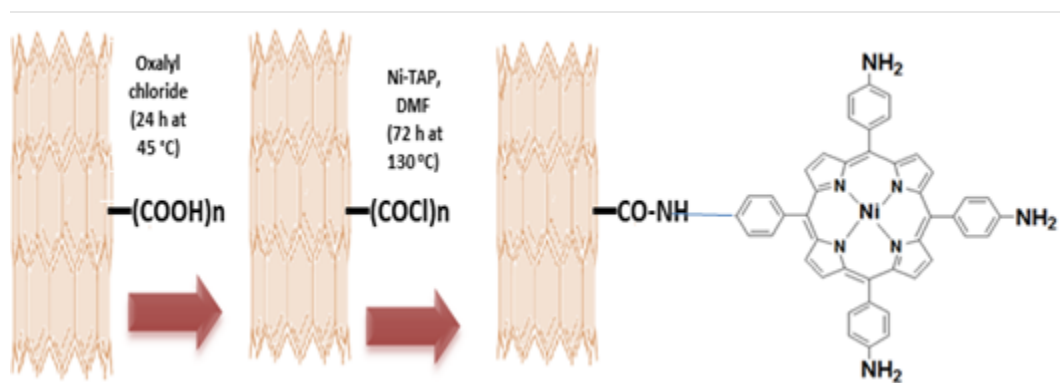
electrical current to electronic pads and batteries without any consequential loss.¹³ SWCNT/porphyrin pairs are used as electrochemical⁹ sensors for different chemical substances such as methanol, acetone, tetrahydrofuran, and ethyl acetate. Moreover, these sensing studies were observed at room temperature by utilizing a network of SWCNTs with metalloporphyrins. Covalently linked nanohybrids can also be used to detect some explosives.^{14,12}

Recently, we reported the change in electronic properties of CNTs by functionalizing them with meso-tetra(4-aminophenyl) porphyrin (TAP) and metal substituted TAP. From Raman spectroscopy, it is evident that MWCNT-TAP exhibit improved electronic property compared to M-TAP (M = Zn or Cu).^{15,17,18} Thus, here we report the covalent functionalization of Ni-TAP by SWCNTs via an amide bond to realize whether there is an increase in the defect peak in Raman due to metal ion substitution only, or this could also be due to the process of acylation. Raman, XPS, and IR spectroscopy identified the edifice of produced nanohybrid. Photo-physical properties of this nano-hybrid were studied through absorption and emission spectroscopy.

EXPERIMENTAL

Synthesis of SWCNT-NiTAP (Nanohybrid (A))

80 mg of SWCNT-COOH was taken along with 15 mL of oxalyl chloride in a double neck round bottom flask and heated at 45 °C for 24 h under argon atmosphere to form acyl chloride functionalized SWCNT-COCl. The remaining oxalyl chloride was removed using a rota-evaporator. 50 mg of Ni-TAP and SWCNT-COCl was dissolved in DMF solvent (15 mL). This reaction mixture was heated in the presence of 1 mL triethylamine (Et₃N) for 3 days at 130 °C under an inert atmosphere. Then the remaining DMF was evaporated using a rotary evaporator. Diethyl ether (80 mL) was added for precipitating the final product. Further, the final residue obtained through the ultra-centrifugation process was washed multiple times with dry THF and chloroform to eliminate the remaining Ni-TAP and other impurities. Each washing cycle consists of ultra-centrifugation and filtration through a nylon membrane. Finally, the residue was washed with distilled water and the product was dried under vacuum. The synthesis of Ni-TAP was confirmed by ¹H NMR spectrum. The synthetic procedure of nano hybrid (A) is outlined in the Scheme-1.



Scheme-1: Synthesis of Nanohybrid (A)

RESULTS AND DISCUSSION

Thermal and Spectroscopic Properties of Nanohybrid (A)

The edifice of nanohybrid (A) was proved by IR spectrum, which is displayed in the Fig.-1. The IR spectrum of SWCNT-COOH included for comparison, SWCNT-COOH illustrates a distinctive peak at 3411 cm⁻¹ which depicts the -O-H bond's vibrational frequency. The peak at 1714 cm⁻¹ in SWCNT-COOH is ascribed to the carbonyl (C=O) stretching vibrational frequency. This carbonyl peak is shifted to 1695 cm⁻¹ in SWCNT-NiTAP, which confirms the -CO-NH amide bond in the nanohybrid. IR spectra of nanohybrid (A) show characteristic peaks at 3318 cm⁻¹ and 1619 cm⁻¹ which correspond to the N-H bond's stretching and deformation vibrations, respectively.²⁰ These variations in IR spectra ratify the formation of SWCNT-NiTAP.

Figure-2 demonstrates the Raman spectrum of nanohybrid (A). Raman spectrum of SWCNT-COOH is also included for comparison. It shows two peaks in the first-order region. A peak that appears around 1300 cm^{-1} is known as D-band and another band that appears around 1500 cm^{-1} is called tangential G-band. In the second-order region, a G'-band (overtone of D-band) appears around 2700 cm^{-1} . There are a series of bands at the lower frequency range between 100 and 300 cm^{-1} which resembles SWCNTs' radial breathing mode (R-band). These bands are unique to SWCNTs which correspond to the expansion and contraction of the CNTs. The intensity of the D-band to that of the G-band (I_D/I_G) ratio is used to measure the carbon nanotube quality. SWCNT-COOH and nanohybrid (A) illustrate I_D/I_G ratios of 0.70 and 0.24 , respectively. The decrease in the I_D/I_G ratio of nanohybrid (A) compared to SWCNT-COOH indicates the improved electronic properties in the nanohybrid (A).¹⁷ The defect in nanohybrid A is less when compared to reported MWCNT-ZnTAP, MWCNT-CuTAP, and SWCNT-ZnTAP.^{15,18} Generally, metal substituted porphyrin nanohybrids show more defects than TAP nanohybrid. This minimized defect in the SWCNTs is due to acylation with oxalyl chloride. There is a higher frequency shift in the position of D band and a lower frequency shift in the position of G band for nanohybrid (A) compared to SWCNT-COOH. This is due to the functionalization of metal substituted porphyrin with SWCNT.

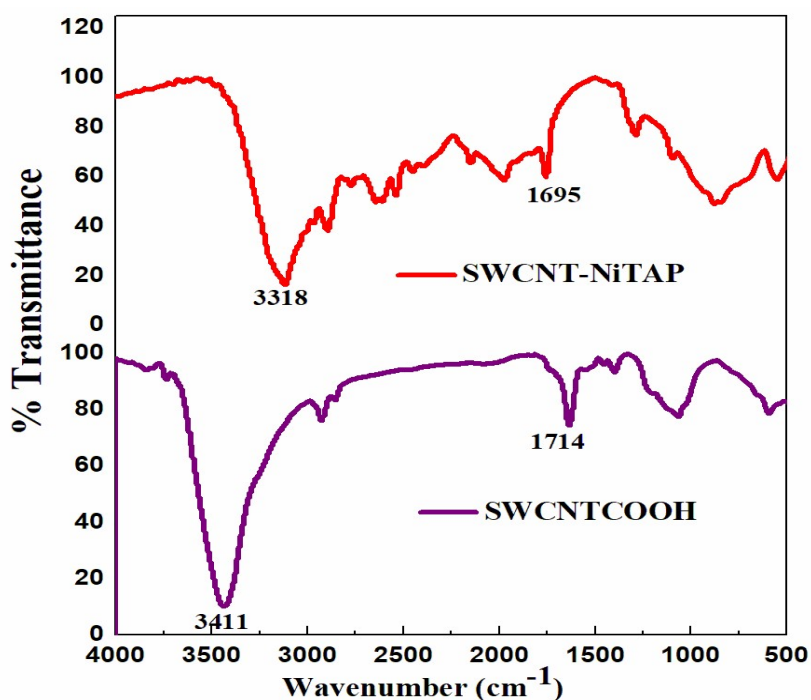


Fig.-1: IR Spectra of SWCNT-COOH and Nanohybrid (A)

Figure-3 depicts the thermogravimetric analysis (TGA) of nanohybrid (A). TGA of SWCNT-COOH, and Ni-TAP are included for evaluation. The TGA plot of SWCNT-COOH depicts loss in weight about $\sim 16\%$ in the $40 - 800\text{ }^{\circ}\text{C}$ temperature range, which confirms its thermal stability. This weight loss is mainly owing to the decarboxylation of the oxidized species.¹⁷ Ni-TAP illustrates a weight loss of $\sim 15\%$ up to $500\text{ }^{\circ}\text{C}$ and subsequently, there is an additional 10% weight loss in $500-800\text{ }^{\circ}\text{C}$ temperature range. Nanohybrid (A) shows 28% weight loss from the $50-800\text{ }^{\circ}\text{C}$ temperature range. This loss in weight is recognized owing to the elimination of Ni-TAP from the nanohybrid, which was covalently connected to the SWCNTs.¹⁸ Therefore, TGA analysis confirms the amount of functionalization of Ni-TAP with SWCNTs.

The X-ray photoelectron spectra (XPS) of SWCNT-NiTAP (A) and SWCNT-COOH are displayed in the Fig.-4. SWCNT-COOH exhibits C 1s, higher intense O 1s peaks, and a lower intense N 1s peak. The feeble peak at 400.10 eV in the spectrum of SWCNT-COOH may be due to the nitric acid utilized for the conversion of SWCNTs to SWCNT-COOH. The higher intensity N 1s peak in the spectrum of

nanohybrid (A) compared to SWCNT-COOH demonstrates the covalent connection of Ni-TAP on SWCNTs.

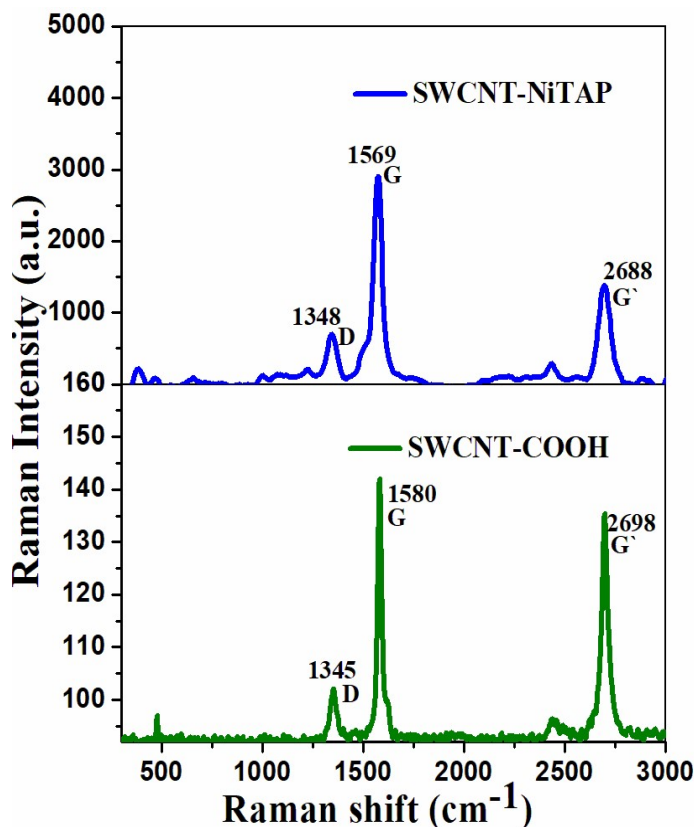


Fig.-2: Raman Spectra of SWCNT-COOH and Nanohybrid (A)

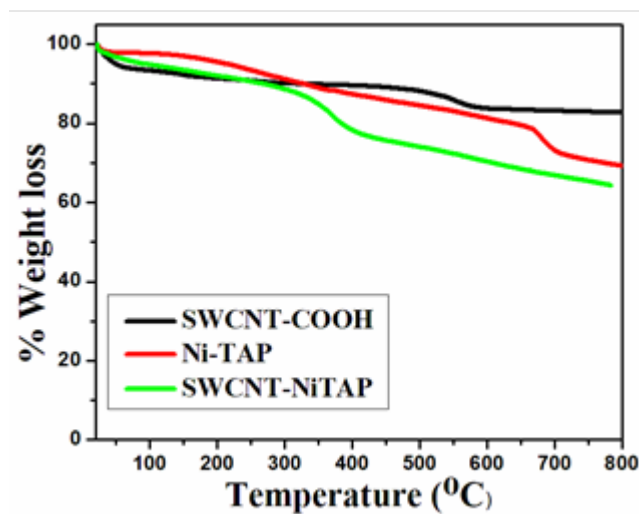


Fig.-3: TGA Plot of SWCNT-COOH, Ni-TAP, and Nanohybrid (A)

The extent of oxidation in SWCNT-COOH was acquired as (C-OH = 9.58 % in 285.83 eV and 3.31 % in 286.40 eV for C=O). Therefore, after the covalent linking of Ni-TAP with SWCNTs, the % of O 1s was reduced compared to SWCNT-COOH. Deconvolution of C 1s and N 1s spectrum of nanohybrid (A) is depicted in the Fig.-5, displayed broad peaks with binding energies of 284.50 - 288.80 eV and 397.15 - 402.60 eV, respectively, which further confirms the functionalization. The extent of Ni-TAP covalently linked with SWCNT was assessed by the peak positions of C-N (284.62 eV) and pyrrolidinic nitrogen

(399.21 eV).²¹ The percentage functionalization of nanohybrid (A) was recognized to be 5.56 % and 3.00 % from the C-N and pyrrolidinic nitrogen binding energy, respectively.

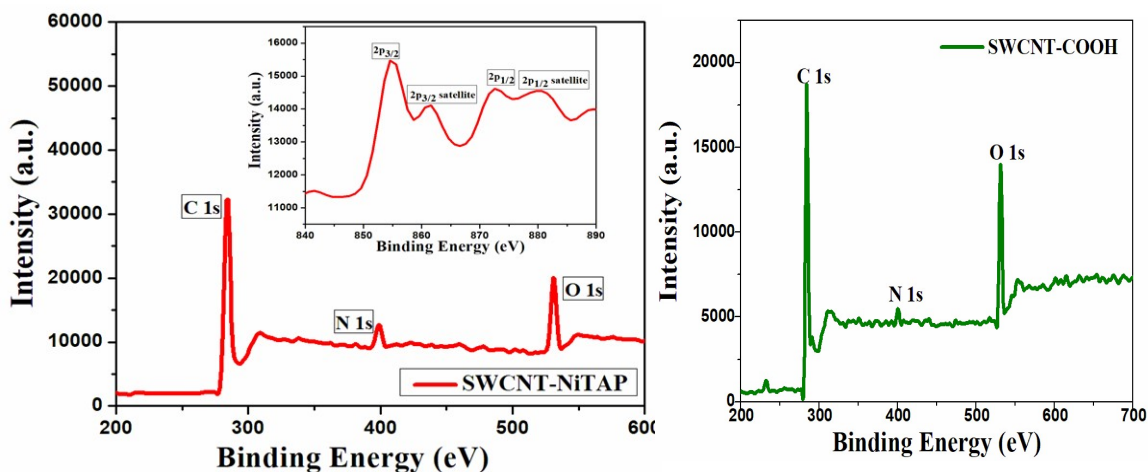


Fig.-4: XPS Spectra of Nanohybrid (A)

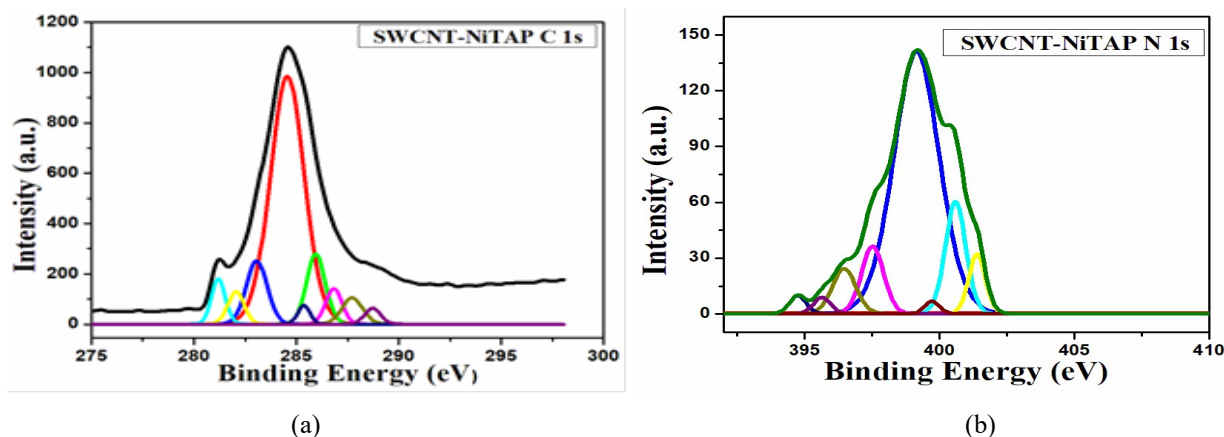


Fig.-5: Deconvolution of (a) Nanohybrid (A) C 1s and (b) Nanohybrid (A) N 1s

Further XPS of nanohybrid (A) depicts some more new peaks associated with Ni $2p_{1/2}$ and Ni $2p_{3/2}$ with binding energies of 872.69 eV and 854.92 eV¹⁸ as displayed in the inlet of Fig.-4. Thus XP spectra ratify the covalent linking of Ni-TAP on SWCNTs.

Morphology Study of Nanohybrid (A) by using TEM

The morphology of SWCNT-COOH and nanohybrid (A) has been examined by HR-TEM analysis as shown in the Fig.-6. it is clear that the tubular morphology has been retained even after Ni-TAP functionalization.

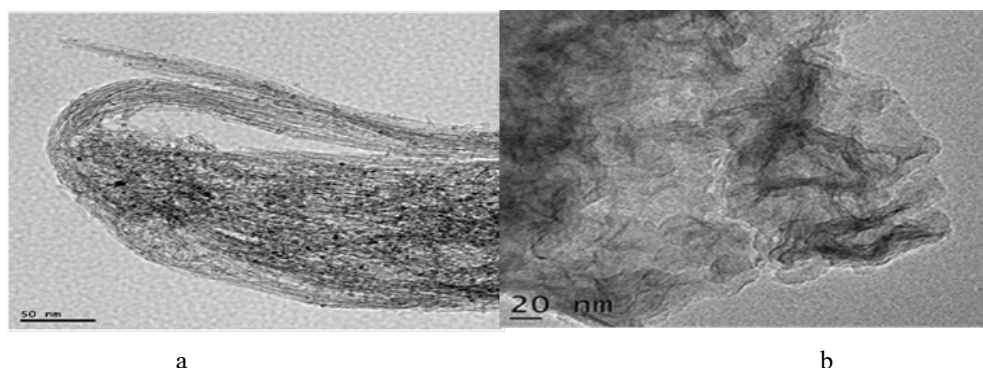


Fig.-6: TEM image of (a) SWCNT-COOH (b) nano hybrid (A)

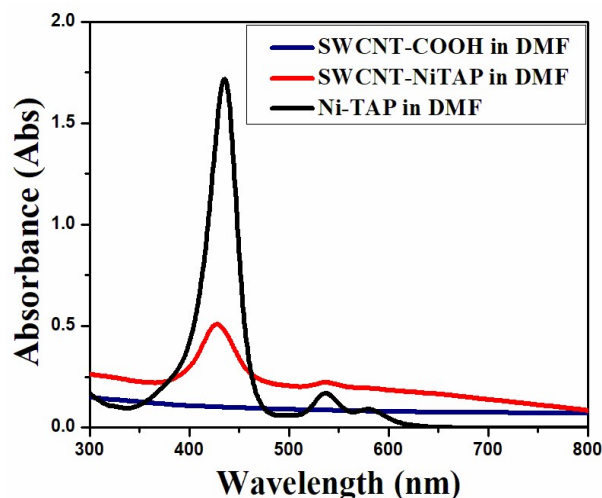


Fig.-7: UV-Vis Absorption Spectra for Ni-TAP (1.034×10^{-4} M), and Nanohybrid (A) (1 mg/100 mL) in DMF Solvent

Linear Optical Properties

The absorption spectrum of nanohybrid (A) in DMF solvent is depicted in the Fig.-7. Absorption spectra of Ni-TAP is also incorporated in Fig.-7 for assessment. Ni-TAP shows two Q bands in the range of 500-700 nm compared to freebase TAP (four Q bands) because of metal ion insertion.¹⁷ This is owing to an enhanced symmetry from D_{2h} to D_{4h} . Soret peak of nanohybrid (A) (426 nm) illustrates hypso-chromic shift as compared to Ni-TAP (435 nm). This blue shift in nanohybrid (A) ratifies the covalent connection of Ni-TAP with SWCNT.¹⁷ Apart from DMF solvent, the solubility of nanohybrid (A) was checked in DMSO and methanol. Nanohybrid (A) displays good solubility in all three solvents. Nanohybrid (A) shows a bathochromic shift (positive solvatochromism) in the absorption band with increasing solvent polarity. The solubility of nanohybrid (A) was confirmed by plotting its Soret band absorbance values versus several concentrations. The linear line was attained with R^2 value of ≈ 0.99 in DMF, ≈ 0.98 in methanol, and ≈ 0.97 in DMSO.

The fluorescence spectrum of nanohybrid (A) in DMF solvent is displayed in the Fig.-8. The fluorescence spectrum of Ni-TAP is also incorporated in the Fig.-8 for comparison. Ni-TAP and nanohybrid (A) are excited at 400 nm. Nanohybrid (A) demonstrates $\sim 86.50\%$ quenching at 475 nm compared to pure Ni-TAP (481 nm). This improved quenching as compared to reported nanohybrids point out that covalent linking enabled an effective electron or energy transfer from Ni-TAP to SWCNTs.^{17, 18}

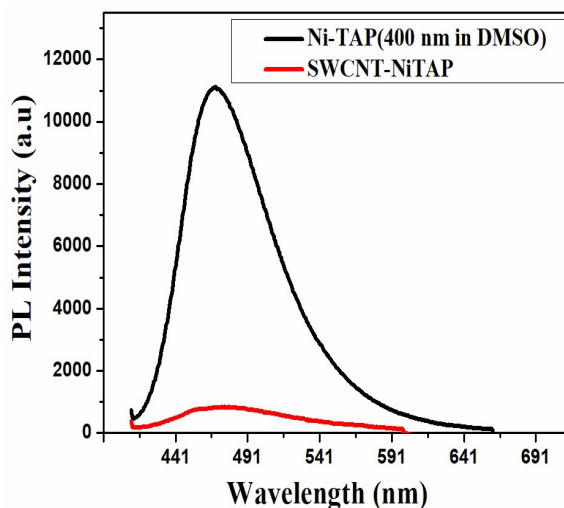


Fig.-8: Fluorescence Spectra of Ni-TAP and Nanohybrid (A) in DMF (Excitation Wavelength = 400 nm).

CONCLUSION

Ni-tetraaminophenylporphyrin was covalently connected to SWCNTs through an amide linkage. Shifting of C=O stretching frequency in FT-IR from 1714 cm⁻¹ to 1695 cm⁻¹ ratifies the covalent linkage of porphyrin with SWCNTs. Raman spectra reveal that the I_D/I_G ratio decreases after Ni-TAP's covalent linkage with SWCNTs compared to SWCNT-COOH, which designates improved electronic properties. This minimized defect in the SWCNTs is due to acylation with oxalyl chloride. TGA plot exemplifies ~28 % weight loss for nanohybrid (A) when heated from 50-800 °C temperature ranges which account for Ni-TAP linked with SWCNTs. The morphology study of this nanohybrid illustrates that the tube-like morphology has remained even after Ni-TAP functionalization of Ni-TAP by SWCNT. Moreover, fluorescence spectra of nanohybrid (A) show that there is ~86.50 % quenching at 475 nm upon excitation at 400 nm. This points out that covalent linking enabled an effective electron or energy transfer from Ni-TAP to SWCNTs.

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