

A Nanohybrid Material of SWNTs Covalently Functionalized with Porphyrin for Light Harvesting Antenna: Synthesis and Photophysical Properties

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Novel covalently porphyrin functionalized single-walled carbon nanotubes (SWNTs) were synthesized using carboxylic group functionalized carbon nanotubes (o-SWNTs) with *meso*-aniline substituted porphyrin. The structure and morphology of this SWNT nanohybrid material were fully characterized with FTIR, Raman, UV-Vis-NIR spectra as well as TGA and TEM measurements. The energy transfer efficiency from porphyrin to SWNTs and porphyrin fluorescence quenching mechanism were studied by means of steady state fluorescence and time-resolved fluorescence measurement. The fast and efficient electron transfer occurring in this nanohybrid illustrates that they can be utilized as a good candidate for light harvesting materials in molecular photonic devices and solar energy utilization.

Keywords: Single Walled Carbon Nanotubes, Light Harvesting, Electron-Transfer, Porphyrin, Fluorescence.

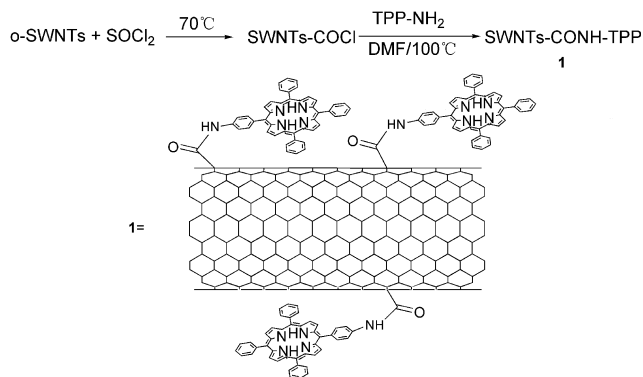
1. INTRODUCTION

Prompted by the truly one-dimensional structure and excellent electron-accepting properties of single-walled carbon nanotubes (SWNTs)¹ and porphyrin's strong light absorbing and electron-donating capability, functionalized SWNTs with porphyrins have been made for potential applications of nano or molecular scale electronics and particularly photovoltaic devices.^{2,3} The strategies for incorporating light absorbing antenna chromophores into SWNTs include both non-covalent^{4,5} and covalent methods.^{6,7} Previous works from other groups^{6,7} and our recent studies⁸ for covalent porphyrin functionalized SWNTs have shown that the linkage modes have significant impact on the energy transfer efficiency and mechanism between the porphyrin molecules and SWNTs. For example, the nanohybrid prepared using direct ester linkage between SWNTs and porphyrins shows strong direct photo-induced electron-transfer (PET) and fluorescence quenching,⁷ but the similar hybrids with longer saturated chains show no or much weaker fluorescence

quenching⁶ and the photo-excited energy is transferred through a space-space energy transfer (ET) mechanism. In our recent study, we have found when the porphyrins were directly connected with SWNTs' conjugation system, the electron-transfer (PET) mechanism occurred and fluorescence was almost completely quenched.⁸ Therefore, the structural arrangement between the tethered porphyrins and SWNTs and their configuration may play a critical role in the intramolecular transduction of excited state energy and results in different deactivation mechanism of photo-excited porphyrin.

Aiming for the preparation of nanohybrid materials with efficient light harvesting capability and better understanding the structure-property relationship for the photo-excited energy transduction mechanism, in this paper we report a novel covalent porphyrin modified SWNTs (1, SWNTs-Por, Scheme 1) with amide bond linkage. The resulting nanohybrid was fully characterized by spectroscopic (UV-Vis-NIR, FTIR, and Raman) and microscopic (TEM) methods. From the investigation of steady state fluorescence and time-resolved fluorescence, we found this nanohybrid showed excellent energy transduction capability with PET mechanism and this material thus could be used for light harvesting antenna material.

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Scheme 1. Schematic view of the porphyrin modified SWNTs 1 prepared in this study.

2. EXPERIMENTAL DETAILS

2.1. Materials

The pristine SWNTs with diameter range of 1.4 ~ 1.7 nm were produced using our previously reported modified arcing procedure.⁹ *N,N*-dimethylformamide (DMF) was distilled freshly from anhydrous calcium sulfate. Thionyl chloride was redistilled before use. Triethylamine and CHCl_3 were dried and distilled from CaH_2 . THF, toluene, and benzene were dried and distilled from sodium under nitrogen. 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (TPP- NH_2)¹⁰ and the carboxylic group functionalized SWNTs (o-SWNTs) was prepared following literature method.¹¹

2.2. Instruments and Measurements

Filtration was performed through nylon membrane (Whatman International Ltd., England/MAGNA, 0.22/0.1 μm , 47 mm) for SWNT purification. Water bath sonication was performed with a KQ-400KDE (400 W, 40 kHz, Kunshan Sonicor Instrument Co., Inc.) sonicator. Raman spectra were measured by a Reinshaw in Via Raman Microscope at room temperature with the 514.5 nm line of an Ar ion laser as the excitation source. FTIR spectra were obtained with a BRUKER TENSOR 27 instrument. All IR samples were prepared as pellets using spectroscopic grade KBr. For thermogravimetric analysis (TGA), a NETZSCH STA 409PC instrument was used and all samples (typically ca. 10 mg) in an alumina pan were heated in dry nitrogen flow (20 sccm) to 960 $^\circ\text{C}$ at a rate of 2 $^\circ\text{C}/\text{min}$. Transmission electron microscope (TEM) images were obtained on a FEI TECNAI-20 instrument operated at 100 kV. UV-Vis-NIR spectra were obtained with a JASCO V-570 spectrometer and UV-Vis spectra were recorded on a VARIAN Cary 300 spectrophotometer using a quartz cell with a path length of 10 mm. Fluorescence spectra were obtained with a VARIAN Cary Eclipse spectrometer. Time-resolved fluorescence decay was performed on a HORIBA NAES-1100 time-resolved

spectrofluorometer (Horiba Ltd., Kyoto, Japan). The excitation wavelength was 420 nm and the emission was collected at 650 nm. The solutions were purged with nitrogen for 20 min before each measurement and all measurements were performed at room temperature.

2.3. Preparation of Covalently Porphyrin Functionalized SWNTs (SWNTs-Por)

The o-SWNTs¹¹ (50 mg) were refluxed with thionyl chloride (30 ml) at 70 $^\circ\text{C}$ for 24 h. After completely removal of excess thionyl chloride through distillation under vacuum, TPP- NH_2 (100 mg) was added to the DMF (8 ml) solution of o-SWNTs-COCl, the mixture was then stirred in the presence of triethylamine (0.5 ml) at 100 $^\circ\text{C}$ for 48 h under nitrogen. The porphyrin functionalized SWNTs 1 (SWNTs-Por) were isolated by washing off the excess of porphyrin with a large amount of chloroform and DMF on nylon membrane (0.22 μm), with the help of sonication. The product (48 mg) was then dried at 60 $^\circ\text{C}$ for 9 h under vacuum. The porphyrin functionalization procedure is shown in Scheme 1.

3. RESULTS AND DISCUSSION

3.1. Characterization of SWNTs-Por Nanohybrid 1

The amide bond connected nanohybrid SWNTs-Por (1) was prepared using standard amide preparation method¹² from SWNTs functionalized with carboxylic groups (o-SWNTs) and TPP- NH_2 . Briefly, o-SWNTs was treated with thionyl chloride and subsequently reacted with TPP- NH_2 to give the porphyrin modified SWNTs (SWNTs-Por 1) as shown in Scheme 1. The Raman spectrum (Fig. 1(B)) of SWNTs-Por exhibits the characteristic SWNTs features: the tangential mode (G-band) at

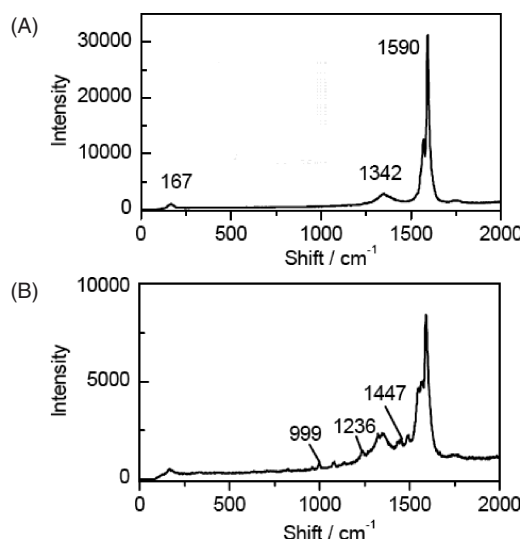


Fig. 1. Raman spectra (514.5 nm excitation) of o-SWNTs (A) and the porphyrin modified SWNTs 1 (B).

1590 cm^{-1} , the disorder mode (D-band) at 1342 cm^{-1} , and the radial breathing mode (RBM) at 167 cm^{-1} . The pattern of these characteristic peaks of SWNTs is similar to that of o-SWNTs and pristine SWNTs, indicating the electronic structure of the SWNTs were preserved upon the attachment of porphyrin. But the relative intensity of disorder mode of SWNTs-Por at 1342 cm^{-1} increased considerably compared with that of o-SWNTs samples as observed in many covalent sidewall functionalization of SWNTs.¹³ Weak peaks at 999, 1081, 1236, 1325, 1447, 1490, 1550 cm^{-1} could be assigned to the covalently attached porphyrin.¹⁴

Figure 2 shows the FTIR spectra of SWNTs before and after porphyrin functionalization. In the spectrum of o-SWNTs (Fig. 2(A)), the peak at 1725 cm^{-1} is attributed to the C=O stretch of the carboxylic group on the walls of SWNTs after the acid-oxidation.¹⁵ In the spectrum of SWNTs-Por (1) (Fig. 2(B)) the C=O peak at 1725 cm^{-1} almost disappeared but a new broad band at 1640 cm^{-1} corresponding to the C=O stretch of amide group emerged.^{12,16} The peak at 1452 cm^{-1} could be assigned to the C-N stretch of amide. New peaks at 1693, 1550, and 722 cm^{-1} are also in consistent with the presence of porphyrin. These results clearly indicate that porphyrin molecules are covalently bonded to SWNTs via the formation of amide bond.

TGA has been used widely for the characterization of functionalized SWNTs.^{8,17} From Figure 3, it can be seen that about 10 wt% loss of o-SWNTs under 300 °C, which was attributed to carboxylic acid groups introduced to the surface of SWNTs during the treatment of nitric acid.¹⁵ Due to the attachment of porphyrin, the gradual weight loss of SWNTs-Por (1 in Fig. 3) starts from about 200 °C and extends to above 600 °C which was ca. 100 °C

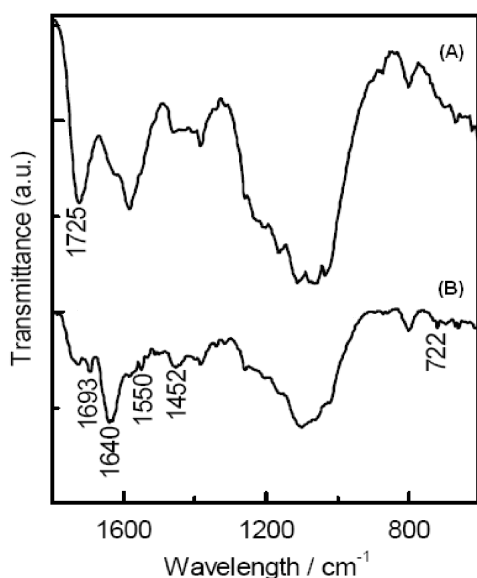


Fig. 2. FTIR spectra of o-SWNTs (A) and the porphyrin modified SWNTs 1 (B).

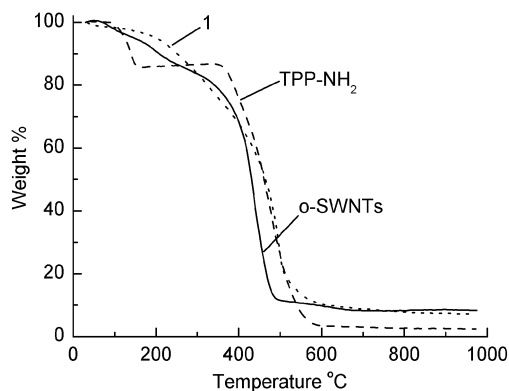


Fig. 3. TGA thermograms of o-SWNTs, TPP-NH₂, and 1 in air (2 °C/min).

higher than that of o-SWNTs. Furthermore, the characteristic weight loss of TPP-NH₂ at 100 °C to 150 °C was no longer observed in Figure 3. These results are consistent with the earlier reports for covalently functionalized SWNTs.^{8,17} The observed weight loss of o-SWNTs, TPP-NH₂, and SWNTs-Por were 91.8%, 97.4%, and 92.5%, respectively. If it could be assumed that the TGA loss of SWNTs-Por is a simple addition of the lose contributions from TPP-NH₂ and SWNTs, the weight percentage of porphyrins in SWNTs-Por can be roughly estimated to be ca. 12.5%.¹⁸ TEM images in Figure 4 offer further evidence for the attachment of TPP-NH₂ on SWNTs. Unlike the smooth sidewall of unmodified SWNTs (o-SWNTs), the TEM image (Fig. 4B) of SWNTs-Por shows the existence of systematic soft materials on the surface of SWNTs. While the unreacted acid groups and the damage caused due to functionalization may also contribute the existence of this systematic soft material, it is more likely caused due to the existence of attached porphyrins

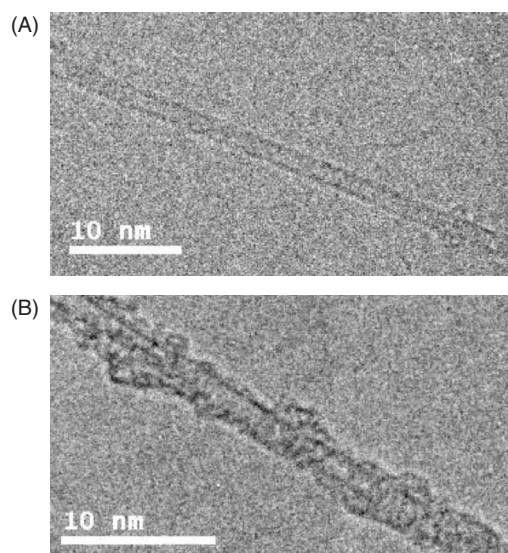


Fig. 4. HRTEM images of unmodified o-SWNTs (A) and porphyrin modified SWNTs 1 (B).

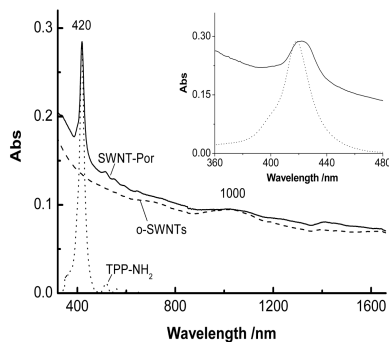


Fig. 5. UV-Vis-NIR spectra of 1 (solid line), o-SWNTs (dashed line), and TPP-NH₂ (dotted line) in DMF. The inset shows the Soret-band region.

as observed in other similar reported materials of functionalized SWNTs.^{6–8}

3.2. Absorption Spectra Investigations

The UV-Vis-NIR absorption of SWNTs-Por (Fig. 5) in DMF showed the unique absorption peaks of porphyrin Soret band at ~420 nm, Q-bands at ~516, 556, 600, 649 nm, and the characteristic broad bands at ~700 and ~1000 nm corresponding to transitions associated with the S₂₂ and M₁₁ bands of SWNTs.¹⁹ Compared with the Soret-band absorption of TPP-NH₂, slight red shift (~2 nm) and notable broadening was observed for SWNTs-Por. Broadening and red-shift of the Soret band for the porphyrin moiety indicate that the amide bonding to SWNTs causes some alteration of the electronic states of porphyrin and there is electronic communication between the two π -systems of SWNTs and porphyrin in the ground states. Noncovalently attached porphyrins on SWNTs do not cause any shift or broadening of the Soret-band except there are other strong interactions (i.e., electrostatic Coulomb force).^{3–5, 20, 21}

To investigate how SWNTs affect the coordination ability of porphyrins attached on SWNTs, the chloroform solution of SWNTs-Por was treated with excessive Zn(OAc)₂·2H₂O saturated methanol solution and the metallation reaction of porphyrin with Zn(II) was monitored with the characteristic peaks of porphyrin and its Zn(II) complex. After the addition of an excessive Zn(OAc)₂·2H₂O saturated methanol solution, the Soret band at ~420 nm decreased gradually and a new peak at ~426 nm emerged simultaneously (Fig. 6(A)), indicating the formation of Zn(II) chelating porphyrin. And the metallation reaction finished in a much longer time (>180 min) than that (10 min) of the model compound TPP-NH₂. Figure 6(B) shows the kinetic data of the metallation with porphyrin. The kinetics of reaction was monitored at 426 nm where the Soret band absorption of the Zn(II) chelating porphyrin locates. Since the Zn(II) was highly in excess, the reaction could be regarded as a pseudo-first order reaction. Thus we could estimate the pseudo-first rate constants of

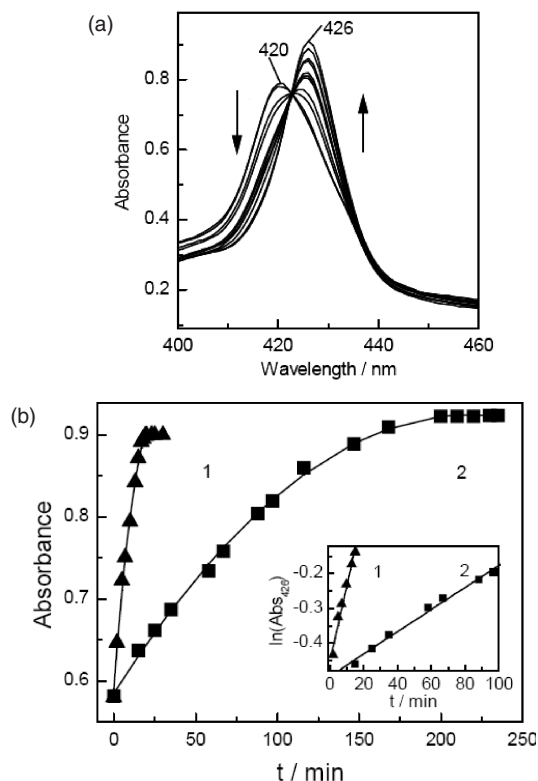


Fig. 6. (A) Changes in absorption spectra of 1 with time (the arrows) in CHCl₃ upon adding excess zinc acetate. (B) Absorbance changes of TPP-NH₂ (1) and 1 (2) at 426 nm after adding excessive zinc acetate. The inset shows the plot of ln(Abs₄₂₆) versus time. The R values for the linear fitting are of 0.989 (1) and 0.995 (2). Since the data for the initial and termination parts generally give more errors, they were not included for the fitting.

the metallation with zinc acetate from the slopes of linear plots of ln(Abs₄₂₆) versus time to be 0.0219 and 0.0032 for TPP-NH₂ and SWNTs-Por, respectively (Fig. 6(B) inset). The R values for the linear fitting are 0.989 and 0.995, respectively. The pseudo-first reaction rate of SWNTs-Por with Zn(II) is only ~1/7 of that of the reaction for free porphyrin with Zn(II). Two factors may contribute this significant rate decrease:

- (1) the anchoring of porphyrin molecules on SWNTs slows down the TPP molecule movement rate and
- (2) the bulky SWNTs around porphyrin molecules hinder or block the insertion of Zn(II) ion into porphyrin molecule.

3.3. Photo-Induced Energy Transfer and Mechanism Studies

Porphyrin is well known as light harvesting antenna in natural photosynthesis systems as well as in artificial donor–acceptor systems and photovoltaic devices²² and a series of porphyrin–fullerene dyads has been intensively studied.^{23, 24} In general SWNTs are good electron acceptors because of its huge π -electron system and high electron affinity,²⁵ and different linkages have shown

strong impact to the porphyrin fluorescence quenching efficiency and energy transfer mechanism.^{6–8} Thus the excited state interaction of porphyrin with SWNTs in this amide covalent linked SWNTs-Por nanohybrid was probed with fluorescence studies. Upon excitation at Soret band (420 nm) of porphyrin moiety, SWNT-Por exhibited >86% fluorescence quenching with subtracting the absorption of SWNTs as compared with that of TPP-NH₂ in DMF (Fig. 7). Similar quenching (>86%) was also observed at other excitation wavelengths (400, 419, 516 nm). Possible pathway for the deactivation of photo-excited porphyrin may be attributed to two competitive processes as mentioned above: energy transfer (ET) and photo-induced electron transfer (PET).^{26,27} Because the emission of porphyrin overlaps with the absorption of SWNTs, so singlet–singlet energy transfer from porphyrin moiety to SWNTs is in principle possible.²⁷ As the energy transfer (ET) generally does not depend on solvent polarity while the electron transfer tends to be sensitive to medium effects,^{6,28} the significant decrease of the fluorescence quantum yield of SWNTs-Por with increasing the solvent polarity (Table I) indicates that the quenching process in our SWNTs-Por nanohybrid is dominated by the excited state electron transfer (PET). In order to further probe electron-transfer interactions in the photoexcited states of SWNTs-Por, time-resolved fluorescence for both the model compound TPP, and SWNTs-Por was performed. For TPP, the reported lifetime obtained using a mono-exponential expression fitting for the fluorescence decay data is 12.8 ns in DMF.⁵ However, for SWNT-Por, an acceptable χ^2 -value (i.e., 1.01) can only be obtained when treating the decay traces with a biexponential fitting function; that is, a long-lived (10.6 ± 0.13 ns) component with 14% share and a short-lived (0.68 ± 0.086 ns) component with 86% share (Fig. 7 inset). The result is consistent with many studies on covalent intramolecular D-A complexes, where the fluorescence decay data usually exhibit two or multiexponential behaviour.^{30–32}

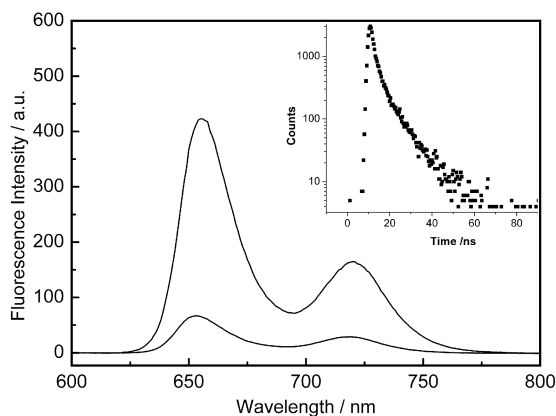


Fig. 7. Fluorescence spectra of DMF solution of TPP-NH₂ (top) and 1 (bottom) with normalizing the excitation wavelength (420 nm) to the same absorbance. Inset shows the fluorescence decays of the SWNT-Por at 650 nm following excitation at 420 nm in DMF.

Table I. Fluorescence quantum yields of 1 in solvents with different polarity.

Solvent	Dielectric constant	Relative Φ_f
DMF	37.06	0.13
THF	7.47	0.40
CHCl ₃	4.89	0.92
Toluene	2.43	1.00 ^a

^aMeasured at 298 K. Solutions were deoxygenated by purging with N₂ before quantum yields were determined. The fluorescence quantum yield of 1 in toluene is 0.020 with reference to TPP (in benzene, $\Phi_f = 0.13$).²⁹

This may be explained that the partially flexible amide bridge between the SWNTs and porphyrin molecules could offer the possibility of several different types of conformation, where the excited state electron transfer efficiency for each of these conformations may be different. It is noteworthy that the minor percent of the longer lifetime is still less than that of the free TPP monomer. The relevant electron transfer rate constant within the photoexcited nanohybrid can be calculated as $(1.38 \pm 0.1) \times 10^9$ s⁻¹ from Eq. (1):

$$k_{\text{ET}} = 1/\tau_f - 1/\tau_f^0 \quad (1)$$

where τ_f^0 is the lifetime of the longer lived component and τ_f is the shorter lifetime observed in the biexponential decay in this nanohybrid.³¹

Concerning earlier work reported covalently or non-covalently porphyrins modified SWNTs, the structure of the hybrid and the actual nature of the linkage between SWNTs and porphyrin plays a decisive role governing the fate of the electronic excited state.^{4–8} Both the bonding and structural arrangement between the tethered porphyrin and SWNTs have an important role in the intramolecular transduction of excited state energy.^{6–8} When the porphyrin molecules directly bonded to SWNTs without other spacer (entry 1 in Table II), the porphyrin fluorescence quenching is 97% in DMF solvent and the energy is transferred through a PET mechanism. Similar efficiency and same mechanism were observed for the ester bonding as the linkage without other spacer (entry 2 in Table II). But a much decreased energy transfer efficiency and an ET mechanism were observed to be dominant for the ester bonding with saturated chain spacer (entries 3 and 4 in Table II). The much difference of fluorescence quenching and energy transfer mechanism for entries 3 and 4 has been studied by Ya-Ping Sun et al. carefully.⁶ While the quenching is not favored by a molecular orbital overlapping through the conjugation between porphyrin and SWNTs due to the saturated chain, the long and flexible chain in entry 3 has made it possible for the porphyrin ring to take a position facing the SWNTs surface and thus the quenching mechanism is an energy transfer (ET). But for the hybrid made in entry 4, only one saturated CH₂ exists between the ester bond and porphyrin molecule, thus it is not possible for the porphyrin ring

Table II. The fluorescence quenching efficiency and mechanism for covalent porphyrin modified SWNTs with different linkages.

Entry	Structure	Fluorescence quenching ratio (solvent)	Quenching mechanism	Ref.
1	SWNTs-(-por) _n	97% (DMF)	PET	[8]
2	SWNTs-(COO-por) _n	96% (CHCl ₃)	PET	[7]
3	SWNTs-[COO-(CH ₂) ₆ -por] _n	30% (THF)	ET	[6]
4	SWNTs-(COO-CH ₂ -por) _n	0% (THF)	—	[6]
5	SWNTs-(CO-NH-por) _n	85% (CHCl ₃) 93% (THF)	PET	this work

to adopt similar configuration for efficient energy transfer and fluorescence quenching. Furthermore, the fluorescence decay of the attached porphyrins in entries 3 and 4 is almost the same to the free porphyrins. For the hybrid made in this work (entry 5), the porphyrin and SWNTs are connected by an amide bond directly, so a similar and almost complete quenching was observed as that for the hybrids made in the entries 1 and 2. Furthermore, it is possible that different conformations can still coexist in solution for the SWNTs-Por hybrid due to the semi-rigidity of the amide bond, which is demonstrated by the observation of the biexponential fluorescence decay. Thus, as we mentioned earlier, for a better light-harvesting or antenna material with porphyrin, the bonding plays an important role for the efficient energy transfer and both the linker between it with the electron-accepting material and the structural arrangement between them need to be considered.

4. CONCLUSION

SWNTs-based donor–acceptor nanohybrid was obtained through covalent functionalization of SWNTs by porphyrin via amide bond and this nanohybrid material was studied with Raman, FTIR, UV-Vis-NIR absorption spectra, TEM and TGA. The steady and time-resolved fluorescence show that the energy of the photo-excited porphyrin was effectively transferred through electron transfer mechanism within this porphyrin functionalized nanohybrid and the linkage between SWNTs and porphyrins plays an important role for the energy transfer efficiency and mechanism.

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