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## Selecting semiconducting single-walled carbon nanotubes by polymer wrapping

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## Chapter 2

# Effect of Medium Dielectric Constant on the Physical Properties of Single-Walled Carbon Nanotubes

*In this chapter, the photophysical properties of semiconducting single walled carbon nanotubes (SWNTs) in different environments are analyzed by steady-state and time-resolved photoluminescence (PL) spectroscopy. The PL emission of SWNTs shows a red shift with the increase of the dielectric constant of the environments. The solvatochromic shift depends on the structural properties of the nanotubes and reaches almost 100 milli-electron volts in the case of (7, 5) tubes. These experimental results allow deriving a relationship between the PL shift and the structure of SWNTs. Moreover, the dynamics of 'bright' excitons in semiconducting SWNTs and the effect of the medium on the decay of the excitons are discussed by using time-resolved spectroscopy.*

J. Gao, W. Gomulya, M. A. Loi, *Chemical Physics* **2013**, 413, 35.

## **2.1 Introduction**

The optical properties of SWNTs are of great importance not only because they can help in the understanding of their fundamental physical properties, but also because of the potential application of SWNTs in nano-photonic devices.<sup>[1-5]</sup> The effect of the environment on the photophysical properties of SWNTs has attracted specific research interest in the last few years. Lefebvre et al. demonstrated blue-shifted PL emission from suspended carbon nanotubes compared to that from dispersed SWNTs.<sup>[6]</sup> Ohno et al.<sup>[7]</sup> and Kappes et al.<sup>[8]</sup> compared the PL emission of suspended (or as-grown) SWNTs in different media and described the PL shifts as the result of dielectric screening effects. The study of the role of the dielectric screening in SWNT photophysics requires that the SWNTs are individually dispersed. In this respect, SWNTs dispersed in aqueous solution have been very important for the study of the exciton physics of carbon nanotubes.<sup>[9-11]</sup> Recently, polyfluorene homo- and co-polymers have attracted specific interests due to their unique selectivity towards semiconducting SWNTs. Moreover, the SWNTs with narrow diameter distribution obtained with poly(9,9-di-n-octylfluorenyl-2,7-diyl) (PFO) show much higher fluorescence quantum yield than the aqueous counterpart.<sup>[12-15]</sup>

In this chapter, we study semiconducting SWNTs excitons in different environments. SWNTs were dispersed in toluene with the aid of PFO, and then mixed with different organic solvents. We observed that the PL peaks of the single nanotubes show a red shift and the emission intensity decreases with increasing of the dielectric constant of the environment. The relationship between the solvatochromic shifts and the structural properties of SWNTs is derived. From the study of the dynamics of 'bright' excitons in semiconducting nanotubes we obtain evidences of structural-dependent fluorescence efficiency of individual carbon nanotubes.

## **2.2 Solvatochromic shift of the SWNT as a function of dielectric constant of different solvents**

Because of the miscibility of toluene, the polymer-wrapped SWNT dispersion can be mixed with many organic solvents with different dielectric constants. In this work, we mixed a PFO-SWNT solution dispersed in toluene with several organic solvents with ratio of 1:9 (v/v). The solvents, their dielectric constants and refractive indices are listed in Table 2.1.

The time-integrated PL spectra of the dispersed SWNTs in various solvents are shown in Figure 2.1. The peak wavelength of each species of SWNTs was obtained by fitting the spectral profile with a Lorentzian line shape. Further analysis, i.e. the peak shifting and the integrated photoluminescence will be discussed later in further detail.

Solvents	Relative dielectric constant ( $\epsilon$ )	Refractive index ( $\eta$ )
cyclohexane	2.02	1.43
p-xylene	2.27	1.5
toluene	2.39	1.5
chlorobenzene	5.62	1.52
chloroform	4.81	1.45
o-dichlorobenzene	10.12	1.55
tetrahydrofuran (THF)	7.5	1.41
dichloromethane	9.1	1.42

Table 2.1 Properties of the solvents in this study.

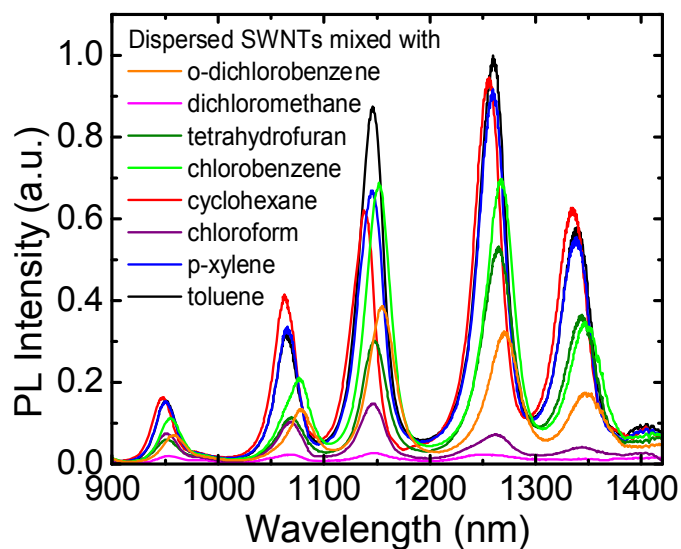


Figure 2.1 PL spectra of dispersed SWNTs in different environments.

Figure 2.2 shows the solvatochromic shift ( $\Delta E_{11}$ ) of 5 kinds of semiconducting SWNTs depending on the dielectric constant of the environment. Solvatochromism refers to the change of fluorescence emission energy due to the change of solvent polarity (or dielectric constant). Dipole-dipole interaction between the fluorophore and solvent molecules lowers the energy of the excited state of the fluorophore. In general, the emission shifts towards lower energy with the increase of the solvent polarity. In this study,  $\Delta E_{11}$  is defined as the difference of the optical transition energy of carbon nanotubes in the specific medium ( $E_{11}^{media}$ ) with respect to that in vacuum ( $E_{11}^{vac}$ ). The optical transitions in vacuum were calculated based on the equation:<sup>[9]</sup>

$$E_{11} = \frac{1241}{A_1 + A_2 d} + A_3 \frac{\cos 3\theta}{d^2} \quad 2.1$$

where  $d$  and  $\theta$  are the diameter and chiral angle of the SWNTs, respectively. The value  $A_1$  is 61.1 nm and  $A_2$  is 113.6 for SWNTs electronic transition in vacuum.

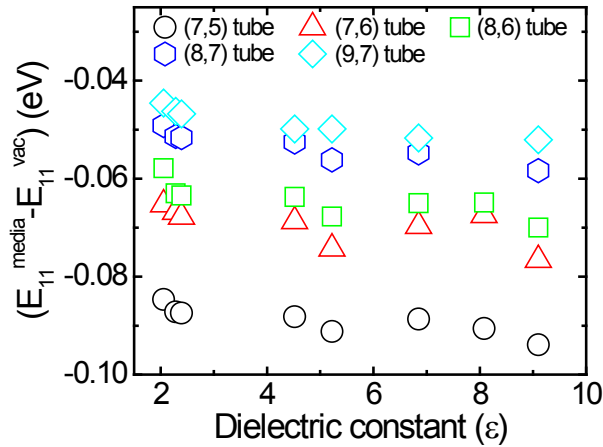


Figure 2.2 Solvatochromic shifts of SWNTs in different environments as a function of dielectric constant.

The value of  $A_3$  depends on the structure of the SWNTs, which is 0.032 eV nm<sup>2</sup> for type I nanotubes ((7, 5), (8, 6) and (9, 7)) and -0.077 eV nm<sup>2</sup> for type II nanotubes ((7, 6) and (8, 7)), respectively. The dielectric constant ( $\epsilon$ ) of the solvent mixtures was calculated by using the equation as reported by Lou et al.<sup>[16]</sup> The PL of dispersed SWNTs shows a red shift up to 0.095 eV with increasing dielectric constant of the environments. This result is in good agreement with a previous report from Ohno et al.<sup>[7]</sup> The second observation is that the smaller diameter nanotubes show larger shifts compared to the larger diameter ones, implying a strong dependence of the solvatochromic shifts of the PL of the SWNTs on the structure of the tubes.

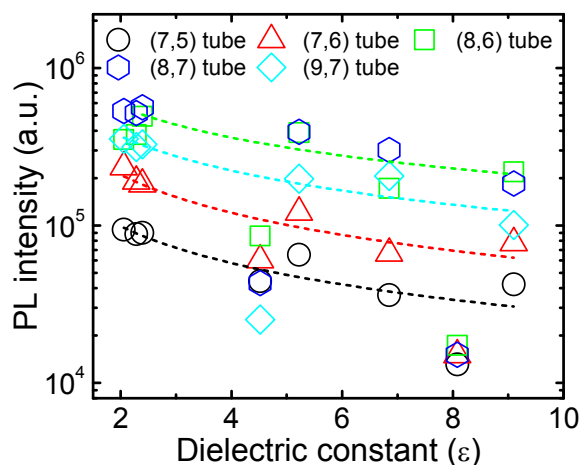


Figure 2.3 PL intensity of SWNTs as a function of dielectric constant. The dashed lines are power law fits.

The PL emission intensity of semiconducting SWNTs ( $I_{SWNT}$ ) in different environments is summarized in Figure 2.3. A clear trend with the intensity of the PL of the single tubes decreasing with the increase of dielectric constant of the media, with no dependence on the SWNT structure is observed. The dependence can be described using a power law  $I_{SWNT} \propto \epsilon^{-0.8}$  (dashed lines in Figure 2.3), which is comparable to that derived by Ziegler et al. ( $I_{SWNT} \propto \epsilon^{-0.5}$ ).<sup>[17]</sup> This observation can be interpreted as the result of a similar “solvent microenvironment” where carbon nanotubes reside in. Two sets of experimental data show significant deviation from the trend that corresponds to the SWNT dispersion mixed with  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ , respectively. Recently, other authors reported a strongly reduced PL intensity of SWNTs dispersed in  $\text{CHCl}_3$ .<sup>[10,17]</sup> These authors attributed the quenching either to the polarity of the solvent or to the presence of SWNT bundles.<sup>[18]</sup> Our results cannot be explained with only the polarity of the solvent. In fact, the emission of SWNTs in THF (mixed with toluene), which is more polar than  $\text{CHCl}_3$ , does not show remarkable deviation from the trend in contrary with what is shown in  $\text{CHCl}_3$  (mixed with toluene). A possible alternative explanation is the instability of the polymer wrapped SWNTs in  $\text{CHCl}_3$ . The superior solubility of PFO in  $\text{CHCl}_3$  compared to toluene might induce aggregation and precipitation of the wrapped SWNTs. It is also known that  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  are not very stable solvents, because they can produce radicals, thus in most commercial solvents, a stabilizer is added. These radicals or stabilizers can also act as recombination centers, lowering the PL intensity.

As we showed above, the solvatochromic shifts of SWNTs depends strongly on the structural properties of nanotubes. Based on Onsager polarity functions, the solvatochromic shifts of carbon nanotubes can be written as:

$$\Delta E_{11} = -K \frac{\Delta\alpha_{11}}{R^3} f(\varepsilon, \eta) \quad 2.2$$

in which  $K$  is the fluctuation parameter,  $\Delta\alpha_{11}$  is the change in polarizability,  $R$  is the SWNT radius,  $f(\varepsilon, \eta)$  is the Onsager polarity function,  $\varepsilon$  is the dielectric constant and  $\eta$  is the refractive index of the solvents.<sup>[19]</sup>

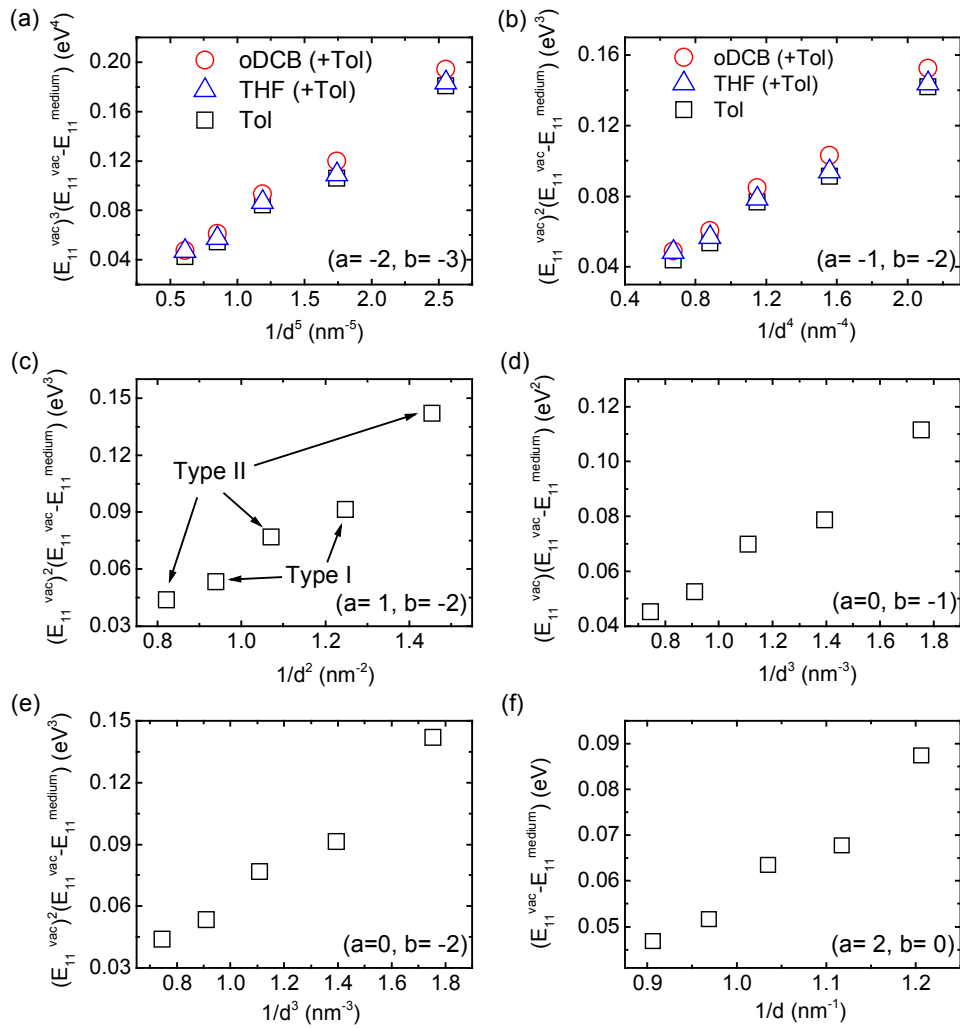


Figure 2.4 Solvatochromic shifts for SWNTs as a function of nanotube structure ( $\alpha_{11} = kR^a(E_{11}^{vac})^b$ ), in which  $(a, b)$  corresponds to (a)  $(-2, -3)$ ;<sup>[17]</sup> (b)  $(-1, -2)$ ;<sup>[9]</sup> (c)  $(1, -2)$ ;<sup>[20]</sup> (d)  $(0, -1)$ ;<sup>[21]</sup> (e)  $(0, -2)$ ;<sup>[22]</sup> (f)  $(2, 0)$ .<sup>[23]</sup>

Being a quasi-1D material, SWNTs show highly anisotropic polarizability. The longitudinal component ( $\alpha_{||}$ ) is more than one order of magnitude larger than the transverse component ( $\alpha_{\perp}$ ).<sup>[24]</sup> As a result, the PL emission from semiconducting SWNTs, also the spectral shifts, is dominated by the longitudinal component. The change in polarizability is also primarily determined by the longitudinal component ( $\Delta\alpha_{||} \approx \alpha_{||}$ ). So far, there have been several reports describing the relationship between the longitudinal component of the polarizability and other physical quantities. One of them expresses the longitudinal polarizability as:  $\alpha_{||} = kR^a(E_{11}^{vac})^b$ , where  $k$  is a constant in a certain environment,  $R$  is the SWNT radius,  $E_{11}^{vac}$  is the optical transition energy in vacuum,  $a$  and  $b$  are integers. However, the values of  $a$  and  $b$  are still controversial and several values have been proposed by different authors.<sup>[10,17,20–23]</sup>

The solvatochromic shifts of the SWNTs in 3 different environments (oDCB (mixed with Tol), THF (mixed with Tol), pure Tol) are demonstrated in Figure 2.4a-b and Figure 2.4c-f, in which  $(a, b)$  correspond to  $(-2, -3)$ ,  $(-1, -2)$ ,  $(1, -2)$ ,  $(0, -1)$ ,  $(0, -2)$  and  $(2, 0)$ , respectively. Surprisingly, scaling relationship between the diameter of the tubes and the solvatochromic shifts can be derived in all the cases and no family dependent behavior was observed (highlighted in Figure 2.4c, (type II,  $(n-m = 3q+1)$ , (7, 6) and (8, 7) tubes) and (type I,  $(n-m = 3q+2)$ , (7, 5), (8, 6) and (9, 7) tubes)). The unexpected agreement is probably due to a narrow diameter distribution of SWNTs species studied.

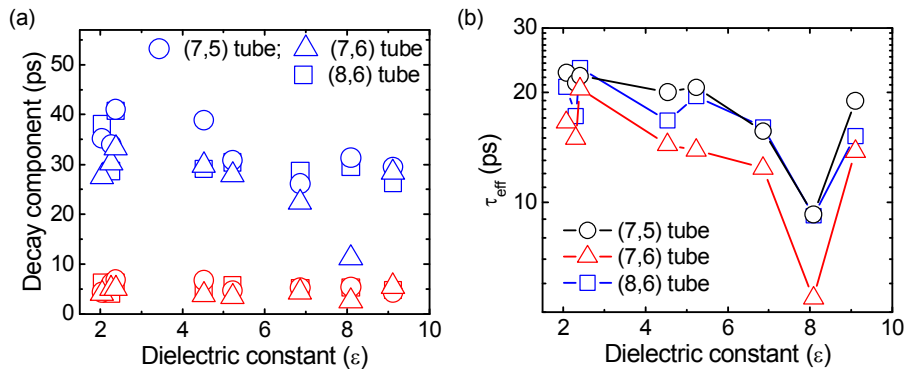


Figure 2.5 (a) Short (red) and long (blue) decay component of (7, 5), (7, 6) and (8, 6) nanotubes as a function of dielectric constant of the environment; (b) effective lifetime of (7, 5), (7, 6) and (8, 6) nanotubes.

The dynamics of the ‘bright’ excitons in SWNTs in different environments was investigated with the aid of a high-resolution streak camera ( $\sim 3$  ps), sensitive in the



near infrared range. The measured PL decays can be accurately fitted with a bi-exponential function:

$$y = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \quad 2.3$$

where  $\tau_1$  and  $\tau_2$  are the short and long decay components, and  $A_1$  and  $A_2$  are the weight of the two components, respectively. This bi-exponential behavior has been observed in the measurements of SWNT ensembles and also in individual SWNT measurements. The short component is dominated by the non-radiative decay due to the presence of “dark” excitonic state, while the long component is much closer to the intrinsic lifetime of carbon nanotubes.<sup>[25]</sup> Figure 2.5a shows the fitted results of the PL decays of (7, 5), (7, 6) and (8, 6) tubes in different media, the error bar for the lifetime data is less than 10% in most cases. We further define an effective lifetime ( $\tau_{eff}$ ) using the average:

$$\tau_{eff} = \frac{(A_1\tau_1 + A_2\tau_2)}{(A_1 + A_2)} \quad 2.4$$

in which the contribution of weight ( $A_1$  and  $A_2$ ) are also taken into account. The effective lifetime of the (7, 5), (7, 6) and (8, 6) nanotubes remain almost constant at 15-20 ps in most environments (Figure 2.5b). An exceptional case is the SWNT dispersion mixed with  $\text{CH}_2\text{Cl}_2$ , where the effective lifetime decreased to less than 10 ps. Another interesting observation is that the effective PL lifetime ( $\tau_{eff}$ ), which is proportional to the fluorescence efficiency of carbon nanotubes, of (7, 6) carbon nanotubes (type II) is always shorter (10%) than that of (7, 5) and (8, 6) tubes (type I), which indicates a structural-dependent PL lifetime and efficiency in SWNTs. A recent study demonstrates that the decay of “bright” excitons in carbon nanotube is influenced by the extrinsic effects such as the defect density, the length of tubes, etc.<sup>[26]</sup> However, we can safely exclude those effects in this study because these three kinds of nanotubes experienced identical treatment and were characterized in the same environments. Carbon nanotubes bundling, which favors energy transfer from large band-gap to small band-gap tubes<sup>[13]</sup> and shorten the lifetime of large band-gap tubes, does not play a role in this case because (7, 5) tubes have larger band gap and longer lifetime than (7, 6) tubes. It then leads to the hypothesis that the lower fluorescence efficiency of (7, 6) tubes compared to (7, 5) and (8, 6) tubes is related to the intrinsic property of carbon nanotubes. This finding is in good agreement with previous studies on individual SWNT<sup>[27,28]</sup> and demonstrates the advantage of PFO wrapped SWNTs for the understanding of the photophysics of SWNTs.

## 2.3 Conclusion

The photophysical properties of semiconducting SWNTs dispersed in different environments having a variety of dielectric constants were studied. The PL emission energy of nanotubes shows red shifts with the increase of the dielectric constant of the media. Time resolved PL results show different effective lifetimes for different species of SWNTs. This is an indication of chirality-dependent fluorescence efficiency.

## 2.4 Methods

**Dispersion of SWNTs.** All the solvents in this study were purchased from Sigma-Aldrich and were used as received: cyclohexane, chloroform ( $\text{CHCl}_3$ ), chlorobenzene, toluene (Tol), o-dichlorobenzene (oDCB), p-xylene, dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), tetrahydrofuran (THF).

HiPCo SWNTs (< 15 wt % ash content) from Unidym were used as received. For the preparation of SWNT dispersions, dry nanotubes were added to 10 mL of polymer solution in a weight ratio of 1 mg SWNT to 3 mg polymer and the mixture was sonicated for 4 h in a tabletop ultrasonic bath (VWR, The Netherlands). After sonication, the crude solution was ultra-centrifuged at 45k rpm (16,000 g) for 1 h. The supernatant ( $\approx 50\%$ ) was removed and mixed with different solvents at the ratio of 1:9 (v/v), then followed by mild sonication for 1 min in order to achieve homogeneity.

**Photoluminescence measurements.** Steady-state and time-resolved photoluminescence (PL) measurements were performed, exciting the solutions at 760 nm by a 150 fs pulsed Kerr mode locked Ti-sapphire laser. PL emission of SWNTs was measured with an InGaAs detector. The time-resolved PL of the SWNT dispersion was recorded by a Hamamatsu streak camera working in synchroscan mode with photocathode sensitive in the near infrared spectral range. All the measurements were performed at room temperature and the spectra were calibrated for the instrumental response.

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