Excitation quenching in polyfluorene polymers bound to (6,5) single-wall carbon nanotubes

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ABSTRACT

Fluorescence quenching of polyfluorene-based polymer (PFO-BPy) attached to single-wall carbon nanotubes (SWNT) has been investigated by means of fluorescence and transient absorption spectroscopy. Fluorescence of SWNT/PFO-BPy complex suspension in chlorobenzene decays nonexponentialy on a time scale from several to several hundreds of picoseconds, and experiences slower depolarization if compared with free polymer in solution. We attribute the slowly quenched and more polarized fluorescence to the polymer tail segments that are not in direct contact with the SWNT. Polymer fluorescence in SWNT/PFO-BPy solid films is quenched about 10 times faster than in suspensions. The initial excited state quenching in films occurs with a 2.3 ps time constant, which we attribute to the polymer chains intimately attached to the SWNT. Slow changes of the spectroscopic properties of the SWNT/PFO-BPy suspensions with time revealed that their aging is associated with the desorption of polymers from SWNT, increasing their tendency to aggregate.

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1. Introduction

Because of their unique electronic properties, single-walled carbon nanotubes (SWNT) are materials with many potential applications for future electronic devices. Fast carrier relaxation, for example, makes them a promising component for photonic devices [1], saturable absorbers for ultrafast lasers [2,3] or optical limiters [4]. There were also attempts to use them in solar cells [5]. SWNT were used as a transparent electrode substituting indium tin oxide layer in organic solar cells [6]. Semiconducting carbon nanotubes have also many attractive properties to be used in active layers of organic solar cells. They have low bandgap, high carrier mobilities [7], fast exciton diffusion and long diffusion length [7], therefore several attempts have been reported to apply them in organic solar cells to improve carrier transport [8,9], or to use as electron acceptors [10] or donors in bulk heterojunction blends [11].

Synthesis of carbon nanotubes usually yields a mixture with more or less random chirality distributions. These are characterized by the distribution of index pairs (n, m) and include both metallic and semiconducting types. Application as well as the spectroscopy of SWNT thus often requires a careful separation of

metallic and semiconducting types by physical or chemical means. The SWNT chirality is particularly important for applications because it determines their electronic structure [12] and, consequently, their optical properties. Specific interactions between several kinds of conjugated polymers and SWNT with a particular chirality enable chirality selection by using tailored polymers [13–15].

These wrapping polymers protect nanotubes from spontaneous aggregation, motivating our interest in the stability of SWNT/polymer complexes. On the other hand, conjugated polymers may also be utilized as a sorting agent and as functional layer. Thus, carbon nanotubes wrapped with polymers may not only be screened from the environment, but their physical and optical properties such as solubility, formation of aggregates, absorption and fluorescence, are modified. Energy and/or charge transfer inside excited SWNT/polymer complex significantly influences their optical and electrical properties and is very important for their applications as photonic materials and components for solar cells.

Here we address excited state dynamics in (6,5)-chirality SWNT wrapped with poly[(9,9-dioctyl uorenyl-2,7-diyl)-alt-co(6,6-2, 2-bipyridine)] (PFO-BPy). Because of narrow energy gap of the SWNT the energy levels of the complex form a so-called type-I heterojunction [16,17] where long-lasting charge separation is

not expected, but formation of short-lived CT states cannot be excluded. On the other hand, energy transfer in type-I heterojunctions is possible, however not necessarily fast and efficient. We demonstrate that fluorescence quenching in SWNT/PFO-BPy complexes occurs by two-step energy transfer from polymer segments in direct contact with the SWNT surface (train-configuration) and from segments of attached polymers extending into the solvent (tail configuration).

2. Materials and methods

2.1. Syntheses and purification of materials

In this study we have investigated four types of samples: pure polymer solutions and SWNT/polymer complex suspensions as well as pure polymer films and films made of SWNT/polymer-complexes. Films were made by spincoating and alternatively by drop-casting. The method for purification and isolation of individual SWNT from raw soot by dispersion with a stabilizing polymer, i.e. PFO-BPy is described in Ref. [15]. In short, SWNT/PFO-BPy complexes are prepared using 7.5 mg of CoMoCAT type SWNT soot (99.9%, Sigma Aldrich) which was mixed with 15.0 mg of PFO-BPy (American Dye Source), suspended in 15 mL toluene (AnalaR NORMAPUR® ACS, VWR International) and sonicated for 7 h at 0 °C [18,19]. Bench-top centrifugation (Biofuge15, Heraeus Sepatech) at 14,000 rpm for 4 min was used to remove bundles and aggregates. To remove excess free polymer from suspensions we filtered 4.0 mL of the clear, yellow supernatant through mixed cellulose ester membranes (Isopore™ Membrane Filters 0.1 μm VCWP, Merck Millipore), with the SWNT network forming on its surface, and rinsed the filter several times with toluene. The filter was then dissolved in acetone and the residue was resuspended in 2.0 mL toluene. The resulting gray–yellow solution was stored at 4 °C to keep polymer desorption prior to experimentation to a minimum. Chlorobenzene SWNT/PFO-BPy solutions in 1 mm cuvettes were investigated. The spin-coated films were prepared from chlorobenzene solution at 1000 rpm. For the fluorescence measurements drop-casted films were used.

2.2. Experimental methods and equipment

Absorption spectra were measured by using the Jasco V670 spectrophotometer. Quartz cuvettes with 1 mm length optical path were used for all optical measurements. The steady-state fluorescence spectra were measured by means of time-correlated single photon counting spectrometer Edinburgh-F900 (Edinburg instruments, United Kingdom). A picosecond pulsed diode EPLED-300 emitting sub-nanosecond (850 ps) pulses was used for the excitation at 300 nm with an average power of 0.08 μW/mm². The pulse repetition rate was 10 MHz. All steady-state fluorescence spectra were corrected for the instrument sensitivity. For the time-resolved fluorescence measurements a spectrometer based on a Hamamatsu C5680 streak camera with M5675 plug-in operating in synchroscan mode was used. Femtosecond Yb:KGW oscillator (Light Conversion Ltd.) was used for the sample excitation. The oscillator produced 80 fs 1030 nm light pulses at 76 MHz repetition rate, which were frequency tripled to 343 nm (HIRO harmonics generator, Light Conversion Ltd.), attenuated, and focused into 100 μm spot on the sample, resulting in about 1 μW/mm² average excitation power. The maximal time resolution of the whole system was about 7 ps.

Transient absorption measurements were performed using ultrafast laser Pharos (Light Conversion Ltd.) with a regenerative amplifier generating 200 kHz frequency, 290 fs duration pulses at 1030 nm wavelength. The proper excitation wavelength at

360 nm was tuned with an optical parametric generator Orpheus and harmonic generator Lyra (Light Conversion Ltd.). Samples were probed with white light supercontinuum generated in 2 mm thick CaCl plate. The spectral range of supercontinuum as well as the detection range of transient absorption spectral dynamics was from 350 nm to 1000 nm. The excitation beam was focused to a spot of about 500 μm diameter while the probe white light supercontinuum beam diameter was around 300 μm.

3. Results and discussion

3.1. Excited state dynamics in solutions

Fig. 1 shows steady-state absorption and time-integrated fluorescence spectra of PFO-BPy polymer and of SWNT/PFO-BPy complexes in chlorobenzene solutions. Both absorption spectra are very similar in the polymer absorption band region. This indicates that the SWNT-polymer coupling in complexes is relatively weak and that the SWNT and polymer retain their individual spectral features. Nevertheless, the absorption band of the polymer is slightly red-shifted and broadened in SWNT/PFO-BPy suspensions suggesting that polymer interaction with the SWNT slightly influences its absorption.

The absorption spectrum of the wrapped SWNT in the spectral region where polymer does not absorb corresponds to the absorption spectrum of SWNT. The absorption band at 574 nm with vibrational replica at 522 nm corresponds to the S_2-transition of the (6,5)-nanotubes, and a weak signal at 651 nm likely corresponds to the S_2 transition of the (7,5) minority species.

The fluorescence spectrum of SWNT/PFO-BPy complexes in solution is very similar to the spectrum of the pure polymer solution. Some differences in the relative intensities of the vibrational replica may be attributed to the polymer distortion and interaction with the SWNT. However, the fluorescence intensity of the polymer attached to the nanotubes was several times lower than that of free polymer. This clearly suggests that excitations of the polymer are quenched by SWNT. It should be noted, that absorption of excitation light and polymer emission light by nanotubes may also additionally reduce fluorescence intensity of the SWNT/PFO-BPy suspension, but this reduction should be minor.
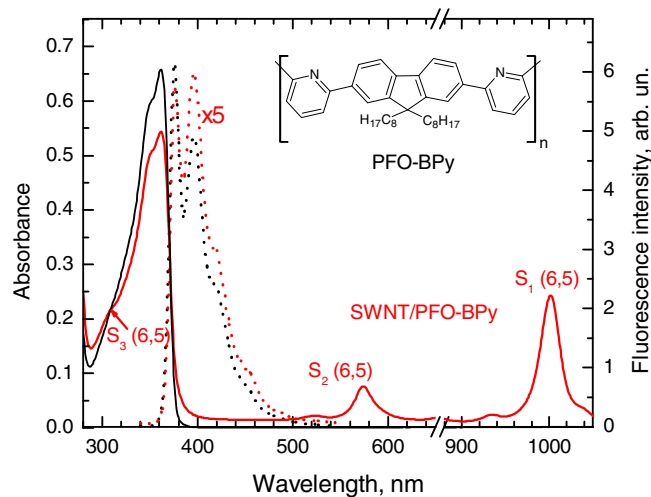

Fig. 1. Absorption (solid lines) and time-integrated fluorescence (doted lines) spectra of pure PFO-BPy (black) and of SWNT/PFO-BPy complexes (red) in chlorobenzene. The S_1, S_2 and S_3 transitions of the (6,5) nanotubes occur at 1001, 574 and 308 nm, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)