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RESEARCH ARTICLE

Noncovalent Functionalization of Carbon Nanotubes by Fluorescent Polypeptides: Supramolecular Conjugates with pH-Dependent Absorbance and Fluorescence

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Fluorescent cut single-walled carbon nanotube (CSWCNT) were prepared by simply mixing CSWCNT with water soluble rhodamine 6G (Rh6G) conjugated poly(3,4-dihydroxyphenylalanine) and poly(L-tyrosine) to form highly stable product with good dispersity in buffer solution. The optical absorbance and fluorescence spectra of the resulting fluorescent CSWCNT display interesting pH-dependent optical properties, emitting strong fluorescence only in acidic environment. Considering the extracellular pH of tumor tissue is acidic, the pH-sensitive conjugates have advantages to sense tumor cells selectively, enabling it to be utilized as a biosensor for detecting cancer cells. The protocol employed to functionalize the CSWCNT with Rh6G conjugated polypeptides in aqueous solution is proven to be direct, fast and easily scalable.

Keywords: Carbon Nanotube, Fluorescence, Poly(3,4-dihydroxyphenylalanine), Poly(L-tyrosine), Rhodamine 6G, pH Sensitivity.

1. INTRODUCTION

Single-walled carbon nanotubes (SWCNTs) continue to gain tremendous interest in recent decades owing to their unique physical, chemical and physiological properties, thus enabling them for use in many applications in the field of nanoscience, nanotechnology and biotechnology.[1–4] Nowadays, two of the most investigated SWCNT-based nanohybrids were prepaeared from the deposition of fluorescein and fluorescent hybrids onto the SWCNT sidewalls, which exhibit interesting pH-dependent optical properties, such as pH-influenced fluorescent selectivity with increased fluorescence and absorption intensity only in acidic environment.[5, 6]

To efficiently synthesize SWCNT-based fluorescent materials, it is vital to activate the graphitic surface of SWCNT that tends to be chemically inert and shows solubility.[5] In this direction, the removal of the toxic metal ions, the decrease of SWCNT length and the covalent decoration of SWCNT sidewall with molecular or polymeric entities provide a direct and effective route to fabricate surface-modified SWCNT derivatives.[7] However, the covalent functionaliztion of SWCNT unavoidably causes the destruction of the band structures of SWCNT and thus undesirably compromises the electronic and mechanical properties.[8, 9] Moreover, the utilization of covalent-modified SWCNT may lead to the non-uniform coverage of additional components that tend to attach at the ends and defective sites of SWCNT, where the concentration of functional moieties are the largest. To this end, liable fabrication of SWCNT-based heterogeneous nanohybrids via non-covalent approaches have attracted immense interest.

In a typical non-covalent process, easily dispersible SWCNT sols can be achieved by deposition of functional molecules onto SWCNT sidewalls through π–π stacking and/or wrapping interactions. Mediated by the deposited molecules, these surface-modified SWCNTs can be further assembled with a variety of nanoparticles or inorganic oxide materials by means of *in situ* synthesis technique, yielding SWCNT-based hybrids that exhibit tailored properties while still reserving nearly all the intrinsic properties of SWCNT.[5] In these non-covalent processes, the sidewall modifier of SWCNT acts as a "bridge" to integrate functional components onto SWCNT sidewalls. Therefore, the molecular composition and structure of modifiers directly decide the efficiency and diversity of the fabrication of novel SWCNT-based nanohybrids.

In this work, water soluble fluorescent rhodamine 6G (Rh6G) conjugated poly(3,4-dihydroxyphenylalanine)

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[p(DOPA)] and poly(L-tyrosine) [p(Tyr)] were chosen as maker for further modification of cut single-walled carbon nanotube (CSWCNT) to preparae a new hybrid material. We present a facile protocol to fabricate the CSWCNT based on a superficially modification of CSWCNT via a non-covalent function with p(DOPA)-Rh6G [or p(Tyr)-Rh6G] in a one-pot reaction. The properties of the resultant fluorescent hybrid materials were studied in deepth and the detailed mechanism was also investigated and discussed.

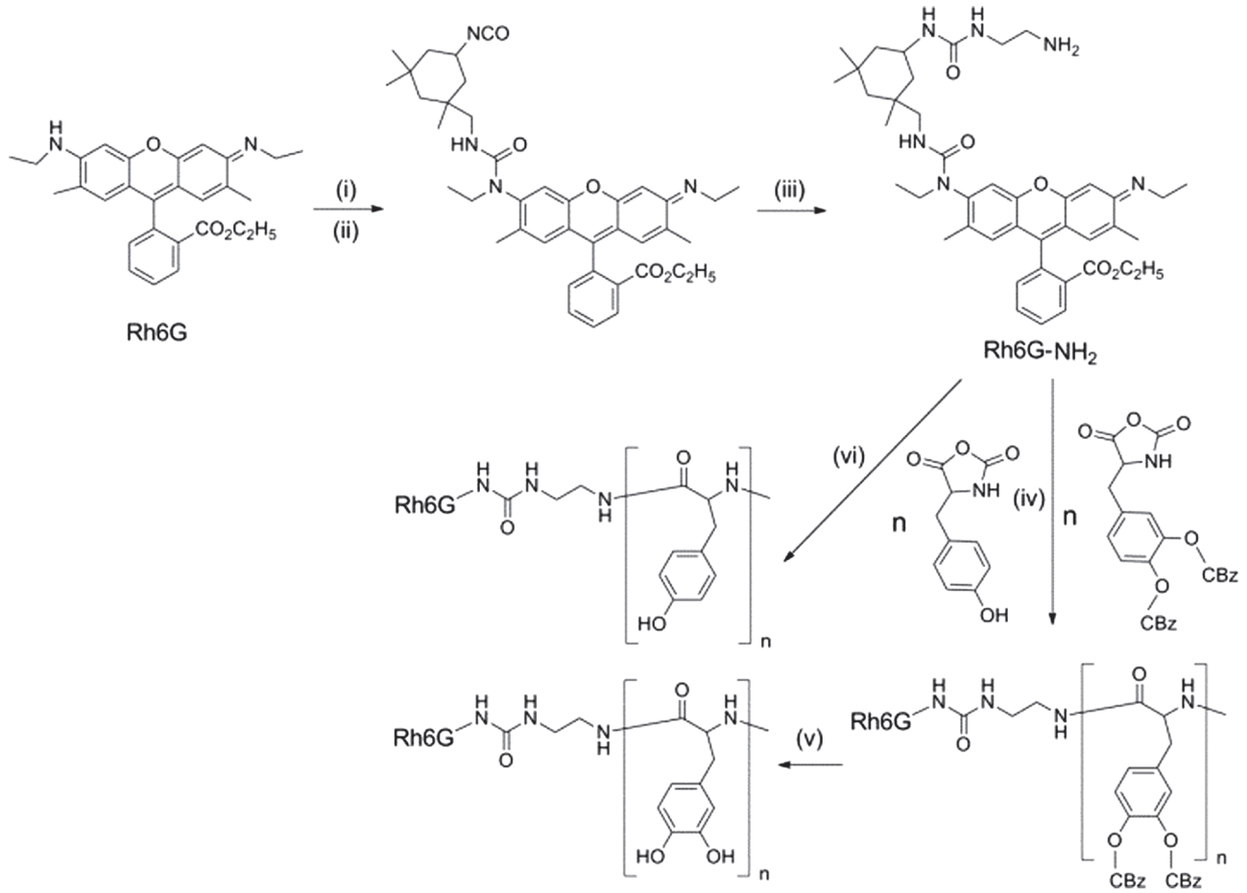
2. EXPERIMENTAL DETAILS

2.1. Materials

Rh6G (98%), isophorone diisocyanate (IPDI, 99%), sodium hydroxide (NaOH, 99%), ethylenediamine (96%), tin octoate (98%), DOPA (99%), L-tyrosine (99%), HBr/acetic acid (30%), trifluoroacetic acid (98%), triphosgene (98%), SWCNT (97%), sulfuric acid (H_2SO_4, 98%), nitric acid (HNO_3, 65%), benzyl chloroformate (CBz-Cl, 98%) and phosphorus pentachloride (PCl_5, 99%) were obtained from Sigma Aldrich, and all of them were used without further purification, dimethylformamide (DMF), tetrahydrofuran (THF) and water were purified according to general procedures before use.

2.2. Characterizations

^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz ^{1}H (100 MHz ^{13}C) spectrometer (Varian Unity Plus), and the fast-atom bombardment mass spectrum (FAB-MS) was recorded on a Jeol JMS DX300 apparatus (Jeol, Tokyo, Japan). Molecular weight (MW) and polydispersity index (PDI) were measured by using a HP 1100 series gel permeation chromatograph (GPC) with polystyrene as the standard, using DMF as the eluent at a flow rate of 1 mL min^{-1}. Samples for transmission electron microscopy (TEM) were deposited onto carbon coated copper electron microscope grids and dried in air. The size, shape and fine structures of nanoparticles (NPs) were investigated using a Hitachi MODEL H-7600 (Nissei, Japan) low resolution and a Jeol 1200 EX II high resolution TEMs. Fourier transform infrared (FTIR) spectra were obtained at a resolution of 1 cm^{-1} with a Shimadzu IR Prestige–21 (Kyoto, Japan) spectrophotometer between



Scheme 1. Synthesis procedures of Rh6G conjugated p(DOPA) and p(Tyr): (i) NaOH (30%); (ii) IPDI, THF, 40 °C, tin octoate, 4 h; (iii) DMF, r,t., ethylenediamine; (iv) and (vi) DMF, 40 °C, 40 h; and (v) HBr/acetic acid, CF_3COOH, CH_2Cl_2.

4000 and 400 cm^{-1}. The IR measurements of the powder samples were performed in the form of KBr pellets. UV-Vis absorption spectra of the samples were recorded at room temperature on a Shimadzu UV-1650PC spectrometer (Kyoto, Japan). All the fluorescence spectra were obtained using a Hitachi spectrofluorometer model F-4500. Zeta potential was conducted using a Malvern Zetasizer 3000 particle size and zeta potential analyzer (Worcestershire, UK) at room temperature.

2.3. Synthesis of Rh6G Amine

The primary amine functionalized Rh6G-NH_2 was synthesized following the procedure in Scheme 1 to obtain a pink solid after vaccum drying. Yield: 86.5%. Melting point = 165 °C, ^{1}H NMR (DMSO-d_6, 400 MHZ): δ 1.19 (*m*, 24 H, –CH_3), 1.83 (*m*, 10 H, –CH_2–), 2.10 (*m*, 3 H, –CH_3), 2.91 (*t*, 2 H, –CH_2–), 3.10 (*m*, 4 H, –CH_2–), 3.15 (*s*, 1 H, CH) 5.03 (*s*, NH), 6.06 (*s*, 2 H, ArH), 6.25 (*s*, 2 H, ArH), 6.93 (1 H, *t*, ArH), 7.45 (*d*, 2 H, ArH), 7.74 (*d*, 1 H, ArH). ^{13}C NMR (DMSO-d_6, 100 MHZ): δ 167.4, 154.0, 151.4, 148.0, 132.0, 131.0, 128.6, 128.0, 124.0, 122.7, 118.6, 105.2, 96.1, 64.6, 43.9, 37.9, 17.4, 14.6. IR (KBr) 3437, 3370, 2963, 2926, 2852, 1682, 1637, 1607, 1518, 1281, 1222, 1007, 815, 748 cm^{-1}. FAB-Mass m/z (%) 726.1 (100) $[M+H]^+$.

2.4. Ring Opening Polymerization (ROP) of α-Amino Acid N-Carboxyanhydride (NCA) (Scheme 1)

DOPA NCA was synthesized in accordance with the previous procedures.[10] Typically, at nitrogen atmosphere, Rh6G-NH_2 (59 mg, 8.15×10^{-5} mol) and carboxybenzyl (CBz) protected DOPA NCA (400 mg, 8.15×10^{-4} mol) were added into DMF (10 mL) solution. The mixture was stirred at 40 °C for 2 days. The residue was purified by precipitation and the CBz groups were deprotected under HBr/acetic acid condition. The resulting water soluble Rh6G conjugated poly(DOPA) [p(DOPA)-Rh6G] was subsequently dried for 10 h at 50 °C under vacuum. ^{1}H NMR (D_2O, 400 MHZ) δ 7.90, 7.54, 7.21, 6.74, 6.71, 6.57 (phenyl ring), 4.59 (OH), 3.52–2.56 (CH_2 and CH derived from p(DOPA)-Rh6G backbone), 2.06–1.81 (CH_2 derived from p(DOPA)-Rh6G backbone), 1.21–0.99 (CH_3), number average molecular weight (M_n) = 5500, PDI:1.03.

The water soluble Rh6G conjugated poly(*L*-tyrosine) [p(Tyr)-Rh6G)] was prepared by the ROP of *L*-tyrosine NCA: ^{1}H NMR (D_2O, 400 MHZ) δ 7.81, 7.05, 6.93, 6.75, 6.50 (phenyl ring), 4.40 (OH), 4.02, 3.83, 3.396, 3.08–2.62 (CH_2 and CH derived from p(Tyr)-Rh6G backbone), 1.90 (CH_2 derived from p(Tyr)-Rh6G backbone), 1.10–1.04 (CH_3), M_n = 7500, PDI = 1.01.

2.5. Cutting and Purification of SWCNT

The cutting and purification of SWCNT was essentially carried out using modified literature procedures.[11] Commercial SWCNT (500 mg) was added into a mixture of H_2SO_4/HNO_3 solution (v/v = 3:1, 200 mL) and exposed to sonication at room temperature for 24 h. The resulting CSWCNT was then thoroughly rinsed with ultrapure water and filtered through a microporous filtration membrane (F = 0.22 mm). Obtained product was redispersed in HNO_3 (2.6 M, 200 mL) and heated at reflux for 24 h, collected by vacuum filtration, and washed several times with ultrapure water to neutrality. The product was then dried under vacuum at 50 °C for 24 h for further use.

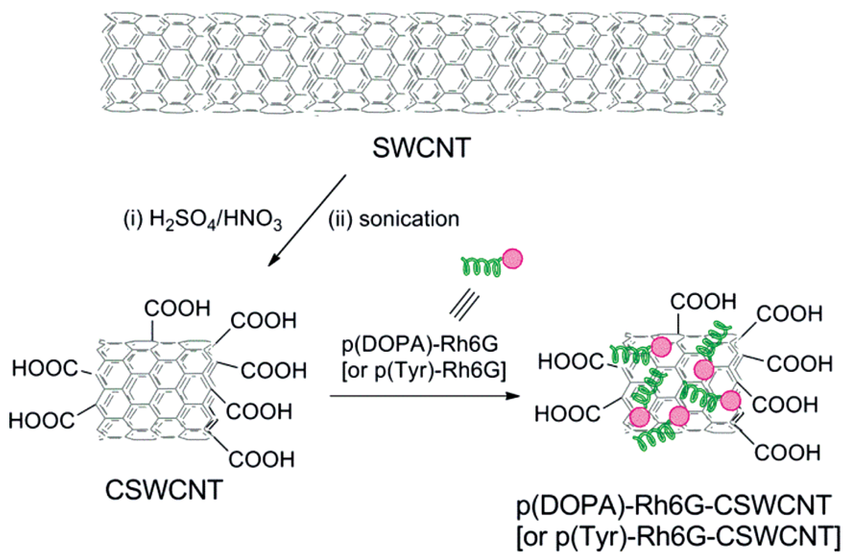


Fig. 1. Organic functionalization of SWCNT. Pristine SWCNT can be treated with acid to cut and generate carboxylic groups at the tip and the sidewall (CSWCNT), and then p(DOPA0-Rh6G [or p(Tyr)-Rh6G] conjugate mixed with CSWCNT to yield noncoordinatively solubilized hybrid in water.

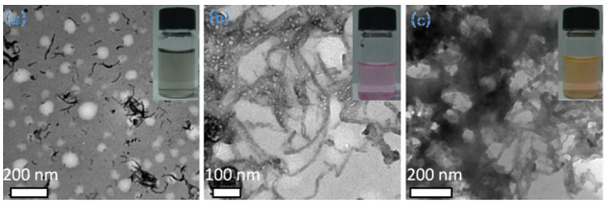


Fig. 2. TEM images of (a) CSWCNT, (b) p(DOPA)-Rh6G-CSWCNT, and (c) p(Tyr)-Rh6G-CSWCNT. Inset of each image illustrates the photograph of water dispersion of each sample.

2.6. Dispersion of CSWCNTs in Aqueous Solution of p(DOPA)-Rh6G [or p(Tyr)-Rh6G)]

The CSWCNT (1.0 mg) was mixed with 5 mg of p(DOPA)-Rh6G [or p(Tyr)-Rh6G)] in phosphate-buffered saline (PBS; 0.01 M, pH 7.4, 10.0 mL). The mixture was sonicated for 10 min, stirred overnight at room temperature, and dialyzed against ultrapure water using a dialysis membrane (molecular weight cut off of 12 K) at room temperature for 24 h to remove free polypeptides.

3. RESULTS AND DISCUSSION

Rhodamine dyes are generally more photostable than fluorescein[12] and are also relatively water soluble compared to naphthalimide-based dyes.[13, 14] We focus on modifying the commercially available dye, Rh6G, because it has an exceptionally high quantum yield (> 0.9) compared to rhodamine B, which typically has quantum yields of the order of 0.3–0.4.[15] Moreover, given very high absorption coeficient of Rh6G (in excess of 100000 M^{-1} cm^{-1}), only a minimal amount of label is necessary, which should minimize any adverse effects that might be caused by the dye label.[16]

In principle, chemical modification of Rh6G may allow this biomedically relevant chromophore to be readily incorporated into polymer chains, either as atom transfer radical polymerization initiators or as a comonomer. The primary amine functionalized Rh6G-NH_2 has been prepared in high yield by reacting Rh6G with IPDI, and ethylenediamine (Scheme 1). The sterically unhindered primary aliphatic amine groups of Rh6G-NH_2 can initiate ROP of NCA to yield polypeptide.[17–19] The control of the degree of polymerization can easily be achieved by variation of the feed ratio NCA/amine (i.e., monomer/initiator ratio). For the cyclization of amino acids, an amino acid suspension was treated in a suitable solvent with 1/3 eq. of triphosgene

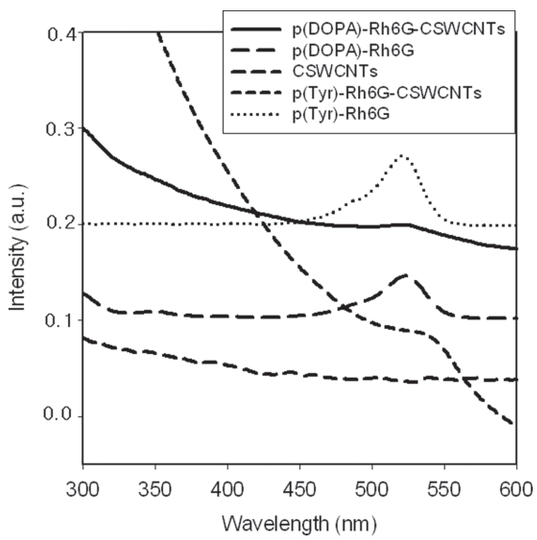


Fig. 3. UV/Vis spectra of CSWCNT, p(DOPA)-Rh6G, p(Tyr)-Rh6G, p(DOPA)-Rh6G-CSWCNT and p(Tyr)-Rh6G-CSWCNT in PBS (2.0 μg mL^{-1}) at pH 7.4.

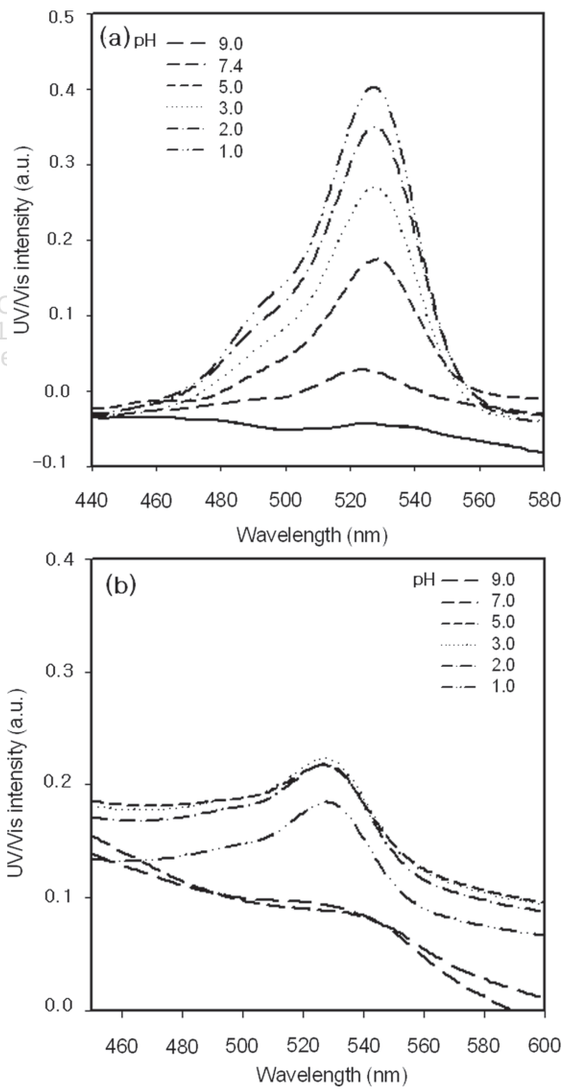


Fig. 4. UV/Vis spectra of (a) p(DOPA)-Rh6G-CSWCNT and (b) p(Tyr)-Rh6G-CSWCNT conjugates in PBS (2.0 μg mL^{-1}) at different pH values.

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at 40–50 °C usually leads to a completely homogeneous solution of the corresponding NCA within 1–3 h. Triphosgene undergoes nucleophilic attack at the carbonyl carbon; the trichloromethoxy (Cl_3CO^-) leaving group dissociates to a chloride anion and a molecule of phosgene, which react immediately. Hence, there is no excess phosgene in solution. Periodic sparging with nitrogen improves product yields by driving the HCl evolved from the reaction medium. The NCAs of CBz protected DOPA and Tyr were prepared in good yield in dioxane as the solvent.

ROP of CBz protected DOPA NCA and Tyr NCA were performed at 40 °C in DMF for 2*d* by using Rh6G-NH_2 as the initiator after controlling the monomer to initiator ratio 100 (Scheme 1). The CBz groups in p(DOPA)-Rh6G was deprotected under the HBr/acetic acid condition. The M_n value of p(DOPA)-Rh6G and p(Tyr)-Rh6G conjugates was 5500 and 7500, respectively. In addition they were characterized by very low PDI value less than 1.03, demonstrating the resulting polymers are very uniform and the initiation step is much faster than the growing step.

The pristine SWCNT tends to cluster into large bundles so that they have very limited solubility in common solvents. Moreover, some metal particles are usually included in the bundles of SWCNT and thus can pose considerable biological toxicity. To eliminate these concerns, the SWCNT used in this study was cut and purified. The cut and purified CSWCNT is much more short in length (usually < 500 nm) and well separated, and formed very small bundles as characterized by TEM observation. After this process, many carboxylic groups are generated mainly on the tip of CSWCNT, which futher enhanced the dispersibility of CSWCNT in buffer solution to form a stable suspension.[11]

Figure 1 shows a schematic diagram for the preparation of the optical hybrid materials. Produced conjugates exhibited ideal dispersity in buffer solution. The combination of p(DOPA)-Rh6G and p(Tyr)-Rh6G molecules with CSWCNT led to roughen the sidewalls of CSWCNT, due to additional coating layers. The average length of the CSWCNT conjugates is about 150 nm determined by TEM observation in Figure 2(a). The p(DOPA)-Rh6G-CSWCNT and p(Tyr)-Rh6G-CSWCNT suspension were stable in PBS without aggregation even after one month (see Figs. 2(b) and (c)). In addition, the zeta potential of nascent CSWCNT suspension is -8.38 mV; however it records to -14.6 mV and -13.7 mV for p(DOPA)-Rh6G-CSWCNT and p(Tyr)-Rh6G-CSWCNT, respectively, indicating that the positively charged polypeptides have been successfully attached to the negatively charged CSWCNTs due to electrostatic interactions in combination with $\pi-\pi$ stackings.[20] When the Rh6G conjugated polypeptides are added to the aqueous CSWCNT solution, non-covalent,

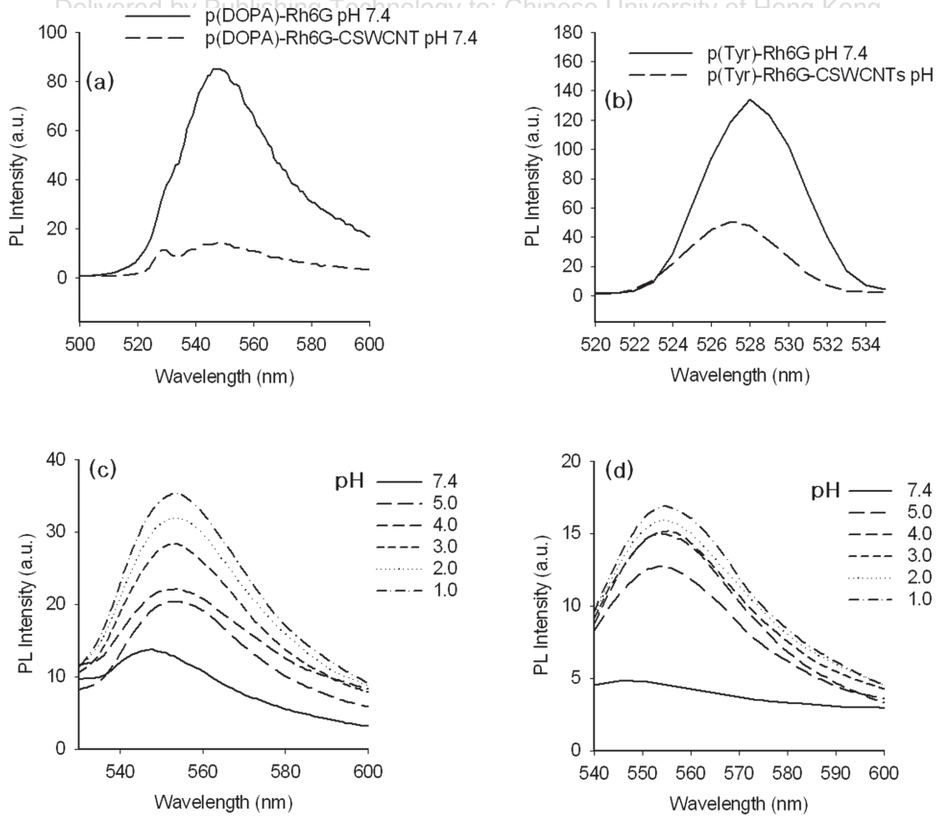

Fig. 5. Photoluminescence spectra of (a) p(DOPA)-Rh6G-CSWCNT and (b) p(Tyr)-Rh6G-CSWCNT in PBS (20 μg mL^{-1}) at pH 7.4; photoluminescence spectra of (c) p(DOPA)-Rh6G-CSWCNT and (d) p(Tyr)-Rh6G-CSWCNT conjugates measured at different pH values.

electrostatic (ion-dipole) interactions exist among the electropositive CSWCNTs and hydroxyl groups of inter- or intrapolypeptide molecules. Such interactions force the polypeptide molecules to be tightly trapped within the voids of CSWCNT to form stable CSWCNT conjugates.

Once Rh6G conjugated polypeptide is conjugated onto CSWCNTs, the interaction between two components is concerted. In PBS at pH 7.4, absorption peaks at 523 and 522 nm corresponding to p(DOPA)-Rh6G and p(Tyr)-Rh6G, respectively, became nortably broadened and shifted to 526 and 542 nm, respectively, for p(DOPA)-Rh6G-CSWCNT and p(Tyr)-Rh6G-CSWCNT (Fig. 3). Interestingly, decreasing pH values, the UV-Vis absorption of p(DOPA)-Rh6G-CSWCNT and p(Tyr)-Rh6G-CSWCNT conjugates became stronger with a continuous red shift (Fig. 4).

It is also shown that the fluorescence of p(DOPA)-Rh6G-CSWCNT and p(Tyr)-Rh6G-CSWCNT conjugates is negligible in comparison to that of pure polypeptide excited at 523 nm at pH 7.4 (Figs. 5(a) and (b)). These results suggest that there are strong interactions between Rh6G conjugated polypeptide and CSWCNT. As in the case of other noncovalently bonded preparations of fluorescent CSWCNTs,[21,22] the energy and electrons from the excitation of polypeptide might directly flow into CSWCNTs and thus quench the fluorescence of polypeptide.[5] Surprisingly, lowering the pH values, the fluorescence of p(DOPA)-Rh6G-CSWCNT and p(Tyr)-Rh6G-CSWCNT conjugates becomes much stronger with a continuous redshift (Fig. 5(c) and (d)). These results clearly indicate that p(DOPA)-Rh6G-CSWCNT and p(Tyr)-Rh6G-CSWCNT conjugates are of distinct pH dependence. The acidic solution might weaken the interactions between polypeptide and CSWCNT, thus a few polypeptide molecules can be dissociated from the sidewalls of CSWCNT at a very low pH. It can be validated by the presence of free polypeptides molecules in the filtrate after the separation of p(DOPA)-Rh6G-CSWCNT and p(Tyr)-Rh6G-CSWCNT conjugates at pH 2.0. Since the Rh6G conjugated polypeptides and CSWCNT are weak acid, the pH-dependent properties of p(DOPA)-Rh6G-CSWCNT and p(Tyr)-Rh6G-CSWCNT conjugates may result from the carboxylate ions and multi-hydroxyl groups in the conjugates. Note that p(DOPA)-Rh6G and p(Tyr)-Rh6G are anchor molecules and the multi-hydroxyl groups and phenyl rings in them induce strong interation with the tip and sidewall of CSWCNT by means of hydrogen bond, electrostatic and $\pi-\pi$ stacking interactions.[23] The Rh6G conjugated polypeptide-CSWCNT hybrid polymers might be a good candidate as a labeling regent for bioanlysis and bioimaging.

4. CONCLUSIONS

p(DOPA)-Rh6G and p(Tyr)-Rh6G with M_n value of 5500 (PDI = 1.03) and 7500 (PDI = 1.01), respectively, were successfully synthesized by the ROP of CBz protected DOPA NCA and Tyr NCA, using Rh6G containing primary amine in structure as an initiator. Simple mixing of the resulting p(DOPA)-Rh6G and p(Tyr)-Rh6G conjugates with CSWCNT resulted in noncovalent interations between p(DOPA)-Rh6G or p(Tyr)-Rh6G and CSWCNT to form highly stable product with good dispersity in buffer solution. The p(DOPA)-Rh6G-CSWCNT and p(Tyr)-Rh6G-CSWCNT conjugates displayed interesting pH-dependent optical properties emitting strong fluorescence only in acidic environment. Considering the extracellular pH of tumor tissue is acidic, pH-sensitive conjugates have advantages to sense tumor cells selectively, which will be a fascinating topic for further study.

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