Quenching effects of gold nanoparticles in nanocomposites formed in water-soluble conjugated polymer nanoreactors

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In this paper we describe the first example of the in situ synthesis of gold nanoparticles (AuNPs) in the presence of a water-soluble conjugated polyfluorene (NPF) presenting pendent ammonium groups, with the polymer acting as an aqueous surfactant and providing fluorescent nanoreactors. Using this approach, we produced well-dispersed NPF-AuNP nanocomposites without the need for any additional reducing agents. The photoluminescence emission intensity of NPF-AuNP nanocomposite solution was quenched to a greater extent upon increasing the concentration of AuNPs, presumably through energy transfer or electron transfer from the fluorescent polymer to the metal nanoparticles. Through variations in the degrees of protonation and deprotonation of the amino groups of NPF at different values of pH, we found that the extent of quenching of AuNPs in NPF-AuNP nanocomposite solutions was directly related to the adsorption and desorption behavior of NPF on the metal surfaces. Transmission electron microscopy revealed that the greatest aggregation of AuNPs in the nanocomposite solution occurred at pH 3, suggesting that the ammonium groups (RNMe\textsubscript{2} at pH 8.5; RNMe\textsubscript{2}H\textsuperscript{+} at pH 3) of the polymer side chains adsorbed onto the AuNP surfaces under these conditions. Distinct time-resolved fluorescence signals of the AuNP-quenched NPF polymers at different values of pH confirmed the interactions between these species.

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1. Introduction

Several methods are available for the preparation of polymers as functional surfactants that interact with metal structures, with applications in the development of biological, optical, and pH sensors [1–5]. Because gold structures on the nanometer size scale exhibit widely size-dependent electronic, chemical, and optical properties [6–8], the surface functionalization of gold nanoparticles (AuNPs) of various sizes has been exploited for a number of applications. AuNPs are commonly synthesized in the aqueous phase through the chemical reduction of chloroaurate precursors (typically chloroauric acid, HAuCl\textsubscript{4}) mediated by sodium citrate, with stabilizers presenting ionic or acidic functional groups often used as surfactants to generate AuNPs with certain characteristic properties [9,10]. Nanocomposites fabricated from polymers and AuNPs have several potential biological applications because of their nontoxicity, biocompatibility, ease of imaging, and the versatile surface chemistry of AuNPs [11,12]. In particular, water-soluble (non-conjugated) polymers containing amino groups can be used as stabilizing and capping agents for AuNPs during the reduction of chloroaurate precursors in aqueous solutions [13,14].

It is well established that metallic surfaces induce strong quenching of molecular fluorescence as a result of energy transfer or electron transfer from the fluorescent molecules to the metals [15,16]. The quenching of the fluorescence of conjugated polymers by AuNPs has been used recently to develop novel fluorescent biosensors for the detection of DNA and for other bio-related applications in aqueous media [17–20]. Moreover, modifications of AuNPs and the polymeric fluorophores are essential for the development of biological labels as well as for optoelectronic applications that take advantage of the strong quenching effects induced by the large total surface areas of the nanoparticles. In chromophore/AuNP nanocomposites, the molecular excitation energy of the chromophores can be transferred efficiently to AuNPs, thereby quenching the emission [21,22]. Several theoretical models of fluorescent nanocomposites have been developed recently to predict the effects of various parameters (e.g., the sizes of AuNPs; the distance between the chromophore and AuNP units) on the fluorescence quenching phenomena [23–27]. The assembly...
of water-soluble conjugated polymer/AuNPs composites, in particular, may provide a route to potential biological applications of AuNPs through improved mechanical, optical, and delivery properties [28–31]. For further bio-developments of nanocomposites, it would be preferable to ensure that the metal nanoparticles and fluorescent conjugated polymers were well dispersed in the aqueous solutions. Herein, we report a facile method for the in situ synthesis of AuNPs in an aqueous solution of a conjugated polyfluorene (NPF) presenting dimethylammonium side chains, where AuNPs were encapsulated within the water-soluble NPF, which acted as a surfactant and also behaved as a water-soluble conjugated polymer nanoreactor. Fig. 1 illustrates the formation of the nanocomposites NPF-AuNPs through reduction of an aqueous solution of chloroauric acid in the presence of the polymer surfactant NPF. Ammonium ions are often used to bind and reduce chloroauric (AuCl₄⁻) ions and stabilize the resulting AuNPs as a result of their high affinities to metallic gold [32,33]. Therefore, polymers containing amino groups (as binding sites) have been used broadly to interact with anionic gold complex ions and as capping agents to control nanoparticle growth [34–36]. The interactions between conjugated polymers and AuNPs in aqueous solutions at different values of pH can lead to different quenching effects in the fluorescent nanocomposites, due to the different degrees of protonation and deprotonation of the amino groups in the gold colloids [37]. The protonation of amino groups of polymers at low pH will lead to the ammonium ions adsorbing on the gold surfaces, resulting in aggregation of AuNPs and, thereby, quench of any fluorescence emission (e.g., for NPF). Fluorescent nanocomposites containing water-soluble conjugated polymers and AuNPs might have practical use in the development of chemosensors or biosensor applications.

2. Experimental

2.1. Materials

All chemicals were purchased from Aldrich and Sigma–Aldrich and used without further purification. Ultrapure filtered water (resistivity: 18.2 MΩ) was used in all experiments. The water-soluble conjugated polymer was synthesized through Suzuki coupling according to pervious reports [38,39]. The synthetic procedure for the preparation of water-soluble conjugated polyfluorene NPF is presented in Scheme 1.

2.2. Synthesis of monomers and polymers

2.2.1. 2,7-Dibromo-9,9-bis(6'-bromohexyl)fluorene (1)

2,7-Dibromofluorene (1 mmol) was added to a mixture of 50 wt % aqueous NaOH (50 mL), tetrabutylammonium bromide (1 mmol), and 1,6-dibromohexane (10 mmol) at 75 °C. After 4 h, the mixture was cooled to room temperature and extracted with CH₂Cl₂. The combined organic extracts were washed successively with water, 0.5 M HCl, water, and brine and then dried (MgSO₄). The solvent was evaporated under reduced pressure and the excess 1,6-dibromohexane was removed through vacuum distillation; the residue was purified chromatographically (SiO₂; hexane/CH₂Cl₂, 10:1) to yield a white solid (59%). ¹H NMR (CDCl₃, ppm), δ: 7.41–7.52 (m, 6H), 3.28–3.33 (t, 4H), 1.52–1.57 (m, 4H), 1.61–1.71 (m, 4H), 1.03–1.26 (m, 8H), 0.53–0.65 (m, 4H).

2.2.2. 2,7-Dibromo-9,9-bis(6'-N,N-dimethylamino)hexyl)fluorene (2)

40 wt% Aqueous dimethylamine (20 mmol, 2 mL) was added dropwise under N₂ to a stirred solution of compound 1 in THF (50 mL) over 1 h at 0 °C and then the mixture was heated under reflux overnight. The reaction mixture was poured into cold water and extracted with CH₂Cl₂; the extracts were dried (MgSO₄) and concentrated under vacuum at 45 °C. The residue was purified by chromatographically (SiO₂; hexane/ETOAc, 5:1) to yield a light-yellow solid (76%). ¹H NMR (CDCl₃, ppm), δ: 7.47–7.57 (m, 6H), 3.30–3.37 (m, 4H), 2.98 (s, 12H), 1.94–2.20 (m, 4H), 1.63–1.74 (m, 4H), 1.07–1.30 (m, 8H), 0.54–0.69 (m, 4H). Anal. Calcd for [C₂₉H₄₂Br₂N₂]; C, 60.21; H, 7.32; N, 4.86; found: C, 60.19; H, 9.14; N, 7.37.

2.2.3. Poly(9,9-bis(6'-N,N-dimethylamino)hexyl)fluorene-co-alt-1,4-phenylene (3)

Compound 2 (10 mmol) and 1,4-benzenediaboronic acid bispicol ester (10 mmol) were dissolved in THF (10 mL) in a 50-mL
two-neck flask. Pd(P\text{-}p\text{-}tolyl)\textsubscript{3} \textsubscript{3} \textsubscript{3} (1 mol % of total monomer concentration) was washed with acetone, dried, and transferred into the flask. 2 M Aqueous K\textsubscript{2}CO\textsubscript{3} and the phase transfer catalyst Aliquat 336 (several drops) were subsequently transferred via cannula into the solution under N\textsubscript{2}. The reaction mixture was stirred at 75 °C for 3 days and then excess amounts of iodobenzene and phenylboronic acid (end-cappers) dissolved in THF (1 mL) were added individually and stirred for 4 h, respectively. The reaction mixture was cooled to 50 °C and added slowly into a vigorously stirred mixture of MeOH (300 mL) and water (100 mL). The pre-polymer (compound 3) was collected by filtration and reprecipitated from MeOH. Yield: 71%. 1H MNR (DMSO-
\textsubscript{d}\textsubscript{6}, ppm), δ:
8.06–7.96 (br, m, 4H), 7.91–7.79 (br, m, 6H), 3.15–3.12 (br, m, 4H), 2.91–2.80 (br, m, 12H), 2.56–2.53 (br, m, 4H), 1.03 (br, m, 16H).

2.2.4. Poly[9,9-bis\{6\text{-}(N,N-dimethylammonium)hexyl\}fluorene-co-alt-1,4-phenylene] dichloride (NPF)

The pre-polymer 3 (0.1 mmol) and 2 M HCl (10 mL) were dissolved in THF (5 mL) at room temperature. After 24 h, diethyl ether was added and the mixture was extracted with water. The aqueous phase was concentrated and the residual NPF was precipitated from EtOH. Yield: 59%, 1H MNR (DMSO-
\textsubscript{d}_{6}, ppm), δ: 8.08–7.99 (br, m, 4H), 7.87 (br, m, 4H), 7.72 (br, m, 2H), 7.35 (br, m, 4H), 2.93–2.86 (br, m, 12H), 2.59–2.55 (br, m, 4H), 1.05 (br, m, 16H). Number-average molecular weight (M\textsubscript{n}): 32,000 g/mol; polydispersity index (PDI): 1.2 (determined using GPC). Decomposition temperature (T\textsubscript{d}): 280 °C (determined by 5% weight loss in TGA). Glass transition temperatures (T\textsubscript{g}) could not be obtained by DSC.

2.3. Growth of AuNPs in aqueous solution

An NPF stock solution (prepared in water at concentrations from 0 to 5 \times 10\textsuperscript{−2} mM) was added to HAuCl\textsubscript{4} solution (2 mM) and then the pH of the solution was adjusted to pH 8.5 by adding 0.1 M NaOH (a few microliters). The solution was placed in a water bath (45 °C) for 4 h, resulting in a solution having a color in the range from light yellow to pink. Transmission electron microscopy (TEM) and UV–vis absorption spectra were used to characterize the shapes and sizes of the nanoparticles. The suspensions of the gold nanoparticles (AuNPs) in the nanocomposite solutions were subsequently adjusted to various values of pH to study the quenching behavior of the nanoparticles. The fluorescence of the nanocomposite (NPF-AuNPs) solutions was quenched to different degrees when different concentrations of the gold precursor were used.

2.4. Measurements and characterization

1H NMR spectra were recorded using a Varian Unity 300 MHz spectrometer and CDCl\textsubscript{3} solutions. Elemental analyses were performed using a HERAEUS CHN-OS RAPID elemental analyzer. Gel permeation chromatography (GPC) was conducted using a Waters 1515 separation module with polystyrene as the standard and DMF as the eluent. Transition temperatures were determined by differential scanning calorimetry (DSC, model: Perkin–Elmer Diamond) under N\textsubscript{2} with a heating and cooling rate of 10 °C/min. Thermogravimetric analyses (TGA) were carried out on a TA Instruments Q500 thermogravimetric analyzer at a heating rate of 20 °C/min under nitrogen. UV–vis absorption spectra of water solutions were recorded using a Jasco V-670 spectrophotometer; photoluminescence (PL) spectra were recorded using a Hitachi F-4500 spectrophotometer. Both types of spectra were recorded from samples in a quartz cell (optical path: 10 mm). PL spectra were measured at the excitonic emission (ca. 379 nm). The PL quenching behavior followed the Stern–Volmer relation

\[ I_0/I = 1 + K_{SV}[Q] \]
where $I_0$ and $I$ are the PL emission intensities of the water-soluble fluorescent conjugated polymer NPF in the absence and presence of the quencher Q (AuNPs), respectively; $K_{SV}$ is the Stern–Volmer quenching constant [40]; and $[Q]$ is the concentration of the quencher.

Transmission electron microscopy (TEM) was performed using a JEOL 2100 electron microscope operated at an acceleration voltage of 200 keV. The samples prepared from aqueous solutions were collected on Cu TEM grids (200 mesh/carbon films) and left to dry completely. Time-resolved photoluminescence (TRP) spectra were measured using a home-built single-photon-counting system. Excitations were performed using a 375-nm diode laser (Picoquant PDL-200, 50 ps fwhm, 2 M Hz). The signals collected at the excitonic emissions of solutions ($\lambda = 421$ nm) were connected to a time-correlated single-photon-counting card (TCSPC, Picoquant Timeharp 200). The emission decay data were analyzed with biexponential kinetics, from which two decay components were derived; the values of the lifetimes ($\tau_1$ and $\tau_2$) and pre-exponential factors ($A_1$ and $A_2$) of NPF in the nanocomposite (NPF-AuNPs) solutions were determined.

3. Results and discussion

3.1. Reduction of HAuCl₄ in the presence of NPF

The water-soluble conjugated polymer NPF was synthesized through Suzuki coupling using procedures described in the literature [34,35]. NPF was used to reduce HAuCl₄ into AuNPs and also as a conjugated polyelectrolyte for fluorescence resonance energy transfer (FRET). The maximum absorption and emission bands of NPF appeared at 379 and 421 nm, respectively (in aqueous solutions). As demonstrated previously [39,41], the presence of ammonium ions on the side chains of NPF provided environments for the formation of AuNPs, with the polymer behaving as both a water-soluble surfactant and a reductant for HAuCl₄. Fig. 1 presents a possible mechanism for the formation of the nanocomposites NPF-AuNPs through the reduction of HAuCl₄ in an aqueous solution of NPF (behaving as a water-soluble conjugated polymer nanoreactor), which contains a conjugated fluoresce backbone and hydrophilic ammonium ions on the side chains. Under these processing conditions, the ammonium groups of NPF were bound electrostatically to the oppositely charged gold precursor ions (AuCl₄⁻). The polymer-bound AuCl₄⁻ ions were slowly reduced into AuNPs under the weakly basic conditions of the aqueous polymer solutions. Signals corresponding to the surface plasmon resonance (SPR) absorption band at 532 nm confirmed the formation of AuNPs. The intensity and wavelength of the maximum absorption ($\lambda_{max}$) SPR bands are known to be correlated with the size and concentration of gold nanoparticles [37]. The presence of different amounts of NPF (from 0 to $5 \times 10^{-2}$ mM) in the aqueous HAuCl₄ solutions resulted in a color change from light yellow (initially) to typical red (finally) after stirring for 4 h, indicating that the side chains of NPF had reduced the AuCl₄⁻ ions to form AuNPs. The UV–vis absorption spectra of the aqueous nanocomposite (NPF-AuNPs) solutions [Fig. 2(a)] featured two maximum absorption bands at 379 and 532 nm, which are characteristic peaks of

![Fig. 2.](image-url) (a) The normalized UV–vis absorption spectra of various NPF-AuNP nano-composites after in situ reduction of aqueous solutions of HAuCl₄ ([AuCl₄⁻] = 2 mM) in the presence of NPF at concentrations of 0, $1.25 \times 10^{-2}$, $2.5 \times 10^{-2}$, and $5 \times 10^{-2}$ mM (b) TEM image of NPF-AuNP nanocomposite containing AuNPs reduced from 2 mM AuCl₄⁻ in an aqueous solution of NPF ($5 \times 10^{-2}$ mM).

![Fig. 3.](image-url) (a) Fluorescence quenching spectra and (b) Stern–Volmer plots of polymer NPF in NPF-AuNP nanocomposites after complete growth (4 h) of AuNPs in aqueous solutions of HAuCl₄ at concentrations from 0 mM to 2.4 mM.
**NPF** and **AuNPs**, respectively. Fig. 2(a) reveals that more AuCl$_4$ ions were reduced in the nanocomposite solution upon increasing the concentration of **NPF** from 0 to 5 × 10$^{-2}$ mM, as indicated by the enhanced intensity of the SPR absorption band of (AuNPs at 532 nm absorption), which also indicated the average sizes of AuNPs. Fig. 2(b) displays the sizes and shapes of AuNPs as examined using TEM; the nanoparticles in NPF-AuNP nanocomposite derived from 2 mM AuCl$_4$ in an aqueous solution of NPF (5 × 10$^{-2}$ mM) exhibited spherical morphologies with particle diameters ranging from 2 to 8 nm (average diameter: 4.5 nm).

### 3.2. Fluorescence of NPF in the presence of AuNPs

Metallic surfaces induce strong quenching of molecular fluorescence as a result of electromagnetic coupling between the metal and the fluorescent molecules; in particular, nanoparticle-induced fluorescence quenching has been studied widely [42–44]. When fluorescent polymers are used as probes for the surface plasmon fields in the vicinity of AuNPs, the fluorescence intensity of the polymers in direct contact with the gold nanostructures is a function of the distance between the probe polymer chains and the metal surfaces [45]. Because the PL emission of our fluorescent conjugated polymer NPF could be quenched by AuNPs, we suspected that the PL emission intensity of NPF-AuNP nanocomposite in solution would decrease upon increasing the concentration of AuNPs. As revealed in Fig. 3(a), the PL emission intensity at 421 nm of the conjugated polymer NPF in the nanocomposite solution decreased upon increasing the concentration of AuCl$_4$ ions (from 0 to 2.4 mM), which was proportional to the concentration of AuNPs formed in situ. Thus, the quenching efficiency of AuNPs in

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**Fig. 4.** (a) PL spectra (excited at the maximum absorption of 379 nm) and (b) UV–vis spectra of aqueous solutions of NPF and its NPF–AuNP nanocomposites at various values of pH. Inset: PL spectra of NPF in different pH conditions.
NPF-AuNP nanocomposite solution varied according to the concentration of HAuCl₄. Fig. 3(b) presents the Stern–Volmer plots of NPF in NPF-AuNP nanocomposites after complete growth of AuNPs in different concentrations of HAuCl₄ (from 0 to 2.4 mM), revealing that the fluorescence of NPF quenched by AuNPs in NPF-AuNP nanocomposite solution had a quenching constant of 4.3 × 10⁷ M⁻¹ (calculated from the linear region at concentrations from 0 mM to 1.4 mM). Therefore, the quantity of AuNPs played an important role in the fluorescence quenching of NPF-AuNP nanocomposite solutions.

3.3. pH-Dependent PL properties of NPF-AuNP nanocomposites

As described in the Experimental section, the color of NPF-AuNP nanocomposite solution changed from light yellow to red when the pH was set at pH 8.5, indicating the formation of AuNPs under weakly basic conditions. Subsequently, we adjusted the pH of NPF-AuNP solution to pH 3 by adding 0.1 M HCl and then to pH 10.4 by adding 0.1 M NaOH. We then subjected the three NPF-AuNP solutions (at pH 3, 8.5, and 10.4) to analyses using UV–vis and fluorescence spectroscopy, TRP, and TEM. Fig. 4(a) and (b) displays the PL (excited at the maximum absorption of 379 nm) and UV–vis absorption spectra, respectively, of the three NPF-AuNP solutions. The maximum PL emission of each aqueous solution in Fig. 4(a) appeared near 420 nm. The inset to Fig. 4(a) reveals that the PL intensities of AuNPs in the absence of AuNPs were not affected by the pH. Upon changing the pH, the fluorescence intensities of NPF-AuNP nanocomposite solutions decreased to different extents, with the largest PL quenching observed at pH 3, presumably because the amino groups on the polymer side chains were highly protonated under these conditions and, therefore, were adsorbed to a greater extent on the AuNP surfaces. The shoulder of PL at ca. 430–460 nm (pH 8.5) reflects the aggregation of polymer chains. At pH 10.4, the amino groups on the polymer side chains were neutralized considerably, leading to lower degrees of adsorption and quenching on the AuNP surfaces.

The UV–vis absorption spectra in Fig. 4(b) reveal the sizes of the dispersed AuNPs under the three values of pH, suggesting their degrees of aggregation. The SPR absorption band of NPF-AuNPs at pH 8.5 appeared near 532 nm. This band for NPF-AuNP solution at pH 3 was red-shifted to 556 nm, due to the greater size of the aggregated AuNPs upon protonation of the amino groups of the polymer. At pH 10.4, the SPR band of NPF-AuNP solution shifted back to 534 nm, due to the lower degree of aggregation of AuNPs. In addition, AuNPs in the initial NPF-AuNP solution at pH 8.5 possessed a spherical morphology with an approximate particle diameter of 4.5 nm [Fig. 2(b)]; greater aggregation of AuNPs (7.8 nm) was evident in the TEM image of NPF-AuNPs at pH 3 [Fig. 5(a)], attributable to the greater degrees of protonation of the amino groups on polymer side chains and adsorption on the AuNP surfaces. At pH 10.4, the TEM image in Fig. 5(b) reveals less aggregation of AuNPs, due to lower content amounts of ammonium groups and resulting decreased adsorption of the polymer onto AuNP surfaces. We suspect that the highly protonated amino groups of the alkylated polyamine played a similarly important role as that of the head groups of cetyltrimethylammonium bromide (CTAB) in the selective adsorption onto AuNP surfaces [41,46]. Likewise, we attribute the formation of our gold nanostructures to the presence of organic layers of alkylammonium chloride units (in an acidic solution) adsorbed onto the Au surface [47]. The ratio of protonated/deprotonated amino groups at a particular value of pH governed the degree of adsorption through the interactions of these groups with the negatively charged surfaces of the inorganic solids. The driving force is electrostatic force and NPF acts as the surfactant of AuNPs and keeps the nanoparticles spherical [48]. The size effect of nanoparticles on TEM images is related to the total surface area of AuNPs. As a result, the effect of the pH on the adsorption of NPF onto AuNPs was a very crucial feature influencing the quenching effect of AuNPs in the fluorescent NPF-AuNP nanocomposite solutions.

3.4. Time-resolved fluorescence analysis of NPF-AuNP solutions

To prove the different quenching effects of AuNPs on the fluorescent nanocomposite solutions, we surveyed the time-resolved PL emissions of NPF-AuNP solutions at different values of pH. Fig. 6 displays the time-resolved fluorescence (TRF) signals of NPF and NPF-AuNP nanocomposite solutions probed at 421 nm (with excitation at 375 nm). Analysis of the fluorescence decays revealed faster decay of the components in NPF-AuNP solutions relative to
those of NPF, suggesting that energy transfer occurred from the fluorescent NPF to AuNPs. Table 1 lists the fluorescence lifetimes obtained through deconvolutions of the instrumental response functions and exponential fittings.

The fluorescence decays of NPF at different degrees of protonation and deprotonation are satisfactorily described by biexponential fittings [45], further improving the analytical accuracy. Therefore, we considered the PL decays of NPF-AuNP solutions to feature two components: a fast process with a decay time \( \tau_1 \) and a slow one with a decay time \( \tau_2 \). Our results suggested that AuNPs tended to quench the fluorescence of NPF through electron transfer and energy transfer processes in NPF-AuNP solutions. A single exponential fitting revealed that the fluorescence lifetime \( \tau_2 \) of NPF was 3.68 ns, corresponding to the lifetime of the S1 state. When AuNPs were introduced into the NPF solutions, the ultrafast decay time constant \( \tau_1 \) appeared in the bieponential decay fittings. At pH 8.5, \( \tau_1 \) was equal to 0.46 ns, with a larger content of the faster-decay component (\( A_1 = 65.4\% \); \( A_2 = 34.5\% \)). More importantly, the presence of the \( \tau_1 \) decay components in NPF-AuNP solutions at different values of pH indicated that the TRF traces consisted of two contributions: one from free NPF \( \tau_2 \) with lower contribution, due to the lower value of \( A_2 \) and the other from its composites \( \tau_1 \) with higher contribution, due to the higher value of \( A_1 \). According to the higher contribution of the faster-decay component \( A_1 \) in NPF-AuNP nanocomposite solutions, the major decay time \( \tau_1 \) decreased to 0.23 ns at pH 3 and increased to 0.32 ns at pH 10.4, consistent with the degrees of interaction between NPF and AuNPs that we deduced from the PL and TEM experiments. The quenching of the TRF signals upon the introduction of AuNPs to form the nanocomposite solutions implied that the metal surfaces produced a charge-transfer emitting state with NPF. Apparently, the interactions between NPF and AuNPs created another fluorescence quenching pathway in which the presence of ammonium receptors led to effective photoelectro energy transfer from NPF to the conjugated main chains of NPF to AuNPs. The observed fluorescence quenching phenomena of the polymeric surfactants presumably reflected the excitation energy transfer from NPF to the metal SPR band of AuNPs. Comparing the fluorescence quenching efficiencies of NPF by the metal surfaces at different values of pH is a useful tool for constructing adsorption and desorption models for NPF on AuNPs.

4. Conclusions

We have prepared a water-soluble conjugated polymer (NPF) presenting side chain ammonium groups for the direct in situ production of AuNPs, thereby facilitating the production of NPF-AuNP nanocomposites without the need to add any typical reducing agents. We observed greater PL quenching behavior of NPF by AuNPs and greater aggregation (TEM of AuNPs) in the nanocomposite solution at pH 3, relative to those at pH 8.5 and 10.4, as a direct result of the greater degree of protonation of the amino groups on the polymer side chains and, therefore, the greater degree of adsorption onto the AuNP surfaces. In contrast to the single exponential fitting of the TRF signals of NPF (with a larger lifetime \( \tau_2 \)), the biexponential decay fittings for NPF-AuNP nanocomposite solutions revealed two PL decay lifetimes \( \tau_1 \) and \( \tau_2 \). Similar to the results of the PL and TEM experiments, the different TRF decay times \( \tau_1 \) for NPF when quenched by AuNPs at different pH values confirmed that stronger interactions existed between NPF and AuNPs at low pH. The pH-dependent variations in the fluorescence quenching behavior in NPF-AuNP nanocomposite solutions might provide a useful tool for constructing adsorption and desorption models for fluorescent water-soluble conjugated polymers on metal nanoparticles; such system might be employed further in forthcoming biotechnological applications.

References

(b) Salata OVJ. Nanobiotechnol; 2004.

(a) Gam-Derouich S, Mahouche-Chergui S, Truong S, Hassen-Chehimi DB, Chehimi MM. Polymer 2011;52:4463–70.
(b) Fuchs AV, Will GD. Polymer 2010;51:2119–24.

(b) Fuchs AV, Will GD. Polymer 2010;51:2119–24.


(a) Bunz UHF, Rotello VM. Angew Chem Int Ed 2010;49:3268–79.