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Photoluminescence quenching effects of surface-modified gold nanoparticles on side-chain polymers containing pyridyl H-acceptors with various lateral polarities

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ABSTRACT

In this study, we used photoluminescence (PL) quenching and transmission electron microscopy (TEM) to study the morphological behavior of hydrogen-bonded (H-bonded) supramolecular assemblies of luminescent H-acceptor polymers and H-donor gold nanoparticles (Au NPs). In fluorescence titration experiments, the lateral Me and MeO substituents on the fluorescent H-acceptor side-chain polymers PBOT1–PBOT3 and PBT1–PBT3 exhibited different electron-donating capabilities, thereby inducing different degrees of H-bonding and dipole–dipole interactions, as evidenced by effective fluorescence quenching upon the addition of surface-modified Au NPs bearing acid and acid-free surfactants (AuSCOOH and AuSC10, respectively). Among all of our tested nanocomposites, the highest Stern–Volmer quenching constant (KSV) was that obtained from the assembly of AuSCOOH with the homopolymer PBOT1. In addition, we developed fittable exponential equations to predict the values of KSV of other fluorescent polymers (containing various molar ratios of pyridyl conjugated units) when titrated with these NP quenchers. The morphologies observed in the TEM images confirmed that fluorescence quenching resulted from the self-assembly of the supramolecular nanocomposites, mediated by H-bonds between the fluorescent H-acceptors of the polymers and the H-donors of the Au NPs presenting acid-modified surfactants.

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1. Introduction

Supramolecular chemistry is a branch of chemistry encompassing systems held together by noncovalent bonds; supramolecular complexes have great potential for use in various rapidly developing fields [1–7]. Recently, directed self-assembly of nanoscale building blocks, mediated by noncovalent interactions (e.g., hydrogen bonding, acid/base proton transfer, electrostatic forces), has led to several interesting developments [8–22]. There is considerable interest in exploiting the fluorescence of conjugated polymers, due to their feasibility for use as highly sensitive chemosensors and biosensors [23–27], which operate based on the different fluorescence quenching abilities induced by supramolecular interactions with particular chemical or biological species [28–31]. Polymers presenting supramolecular receptor groups (e.g., crown ethers, pyridine derivatives and ionic groups) from their side or main chains have been used for the sensing of ions and biological moieties [32–37]. The development of supramolecular assemblies of fluorescent side-chain conjugated polymers, capable of exhibiting either chromogenic or fluorogenic responses in response to noncovalent interactions, has attracted much recent research interest [38–41].

The self-assembly of nanocomposites from nanoparticles (NPs) and fluorescent polymers is a direct means of incorporating the unique physical properties of NPs into...
useful functional materials [42–45]. Due to their stability and biocompatibility, gold (Au) NPs surface-modified with organic layers (such as triphenylene and cyclodextrin surfactants) are highly attractive models for the applications of nanocomposites and biosensors [46,47]. Many high-performance fluorescence assays for the optical sensing of important biological ions and molecules have been designed to take advantage of the superquenching ability of Au NPs. Notably, Au NPs can be functionalized with a variety of monolayer structures so that they become soluble in water or organic solvents. Rotello et al. have widely investigated the synthesis and self-assembly of Au NPs with inherent optical properties [16–22]. Starting with thiol-passivated Au NPs, they used thermal ripening and the Murray place reaction to create NPs comprising highly monodisperse cores surface-modified with carboxylic acid-functionalized monolayers. Murray et al. studied the quenching of fluorophores attached to monolayer-protected Au NPs, mediated by electron transfer from the exited fluorophores to the Au NPs [48]. Direct binding between a fluorophore and a metal surface often results in quenching of the fluorophore’s excited states through both energy transfer and electron transfer processes [49]. Moreover, the Au NPs in the quenched nanocomposites (containing fluorophores) can be replaced by other metal ions to different degrees, as a result of stronger re-coordination or re-complexation of the metal ions with the fluorophores, thereby restoring the fluorescence of the chromophores and providing chemosensors that function through a two-stage self-assembly process [50,51]. In addition, the Au NPs of quenched nanocomposites have also been reacted with reduced glutathione in the presence of a glutathione reductase enzyme; the subsequent recovery of the fluorescence of the chromophores allowed these systems to behave as biosensors [52].

In a previous study, we explored the supramolecular assembly of nanocomposites of fluorescent copolymers presenting proton acceptors (H-acceptors) and surface-functionalized Au NPs presenting donor donors (H-donors), in terms of both their photoluminescence (PL) quenching phenomena and transmission electron microscopy (TEM) morphologies [53]. Competition between the H-donors of the acid pendent units of the copolymers and the acid surfactants of the Au NPs complicated that investigation of those supramolecular nanocomposites. Therefore, in this study, we replaced the acidic H-donor moieties of the previous self–H-bonded copolymer (bearing both H-acceptor and H-donor moieties) with carbazole monomers to construct (H-acceptor only) fluorescent side-chain polymers presenting pendant pyridyl H-acceptors at various copolymeric molar ratios (100, 60, and 30 mol%) with lateral Me and MeO substituents groups. As indicated in Fig. 1, we have generated supramolecular assemblies of H-bonded nanocomposites through the interactions of the carboxylic acid surfactants (proton donors) of the surface-modified AuSCOOH NPs and the pyridyl groups (proton acceptors) of laterally MeO- and Me-substituted polymers (PBT1–PBT3 and PBT3–PBT3, respectively). The fluorescent side-chain polymers PBT1–PBT3 and PBT3–PBT3 exhibited various electron-donating capabilities, thereby inducing different proton acceptor effects when treated with the surface-functionalized Au NPs AuSC10 and AuSC10 (presenting acid and acid-free surfactants, respectively); therefore, the side-chain conjugated polymers PBT1–PBT3 and PBT1–PBT3 bearing fluorescent pyridyl H-acceptor pendant units not only behave as highly selective chemosensors for acid-functionalized Au NPs but also exhibit distinct fluorescent quenching effects upon the addition of surface-functionalized Au NPs (i.e., AuSCOOH and AuSC10, presenting acid and acid-free surfactants, respectively).

We used this approach to develop fitable exponential equations to predict the Stern–Volmer (SV) quenching constants for a diverse range of fluorescent copolymers (containing various molar ratios of pyridyl H-acceptors and different lateral functional groups) when titrated with different NP quenchers. Finally, the results of the PL titrations of the SV quenching constants suggested the optimum quenching mechanism between the fluorescent copolymers and the NPs, which may facilitate the selection of the best operating conditions (with the largest quenching effect) for the preparation of nanocomposites for the first recognition stage, with recovery of the fluorescence of the chromophores (with the strongest re-emitting effect) upon re-coordination (or re-complexation) of metal ions (or biomolecules) with the fluorophores in the second sensing stage.

2. Experimental section

2.1. Materials

Chemicals and solvents were reagent grades and purchased from Aldrich, ACROS, TCI, and Lancaster Chemical Co. Dichloromathane and THF were distilled to keep anhydrous before use. The other chemicals were used without further purification. The synthetic routes of proton acceptor polymers PBT1–PBT3 and PBT1–PBT3 (as shown in Fig. 2) were reported in our previous results [54,55]. The chemical structures of all products were confirmed by 1H NMR spectroscopy and elemental analyses.

2.2. Synthesis of surface-functionalized gold nanoparticles AuSC10 and AuSCOOH

The surface-functionalized gold nanoparticles (AuSC10 bearing acid-free surfactants) used in this study were prepared through standard Brust–Schiffrin methodology [57]. Hydrogen tetrachloroaurate aqueous solution (30 mL, 30 mmol) was mixed with tetractylammonium bromide (TOAB) in toluene solution (80 mL, 50 mmol). The two-phase mixture was vigorously stirred until all tetrachloroaurate was transferred into the organic layer, and then dodecanethiol (20 μL) was added to the organic phase. A freshly prepared aqueous solution of sodium borohydride (25 mL, 0.4 mol) was slowly added with vigorous stirring. After further stirring for 3 h, the organic phase was separated, and the standard Brust reaction mixture was evaporated without removing TOAB and dried completely under reduced pressure. The black solid obtained was heat-treated at 165°C at a heating rate of 2 °C/min and...
held at this temperature for 30 min [58]. The thermally ‘ripened’ product was dissolved in toluene and washed with methanol to remove excess thiol ligands and TOAB, then AuSC10 nanoparticles with alkyl surfactants were obtained. In the subsequent Murray place exchange reaction [59], AuSC10 nanoparticles (60 mg) were combined with the proper amount of 11-mercaptoundecanoic acid in dichloromethane (3 mg of AuSC10/mL) and reacted for 48 h. After the exchange reaction was completed, the reaction mixture was concentrated using a rotary evaporator. After washing these products with a large amount of ethanol and acetone, no further purifications were conducted on these samples. Then, the acid-functionalized gold nanoparticles (AuSCOOH) with a diameter ca. 5–6 nm were obtained, and the monolayer compositions of AuSCOOH nanoparticles with both acid and alkyl surfactants were characterized by 1H NMR featured 79% decanethiol and 21% carboxylic acid thiol functionalities [60–62]. In our studies of nanocomposites, both THF-soluble gold nanoparticles, i.e., alkyl-functionalized gold nanoparticles (AuSC10 bearing acid-free surfactants) and acid-functionalized gold nanoparticles (AuSCOOH bearing acid surfactants), were used.

2.3. Preparation of nanocomposites consisting of gold nanoparticles and polymers

Nanocomposites were prepared by mixing solutions (0.5 mg/ml) of H-acceptor polymers PBT1–PBT3 and PBOT1–PBOT3 in THF (2 mg/ml) with surface-functionalized gold nanoparticles AuSCOOH and AuSC10, which contain acid and acid-free surfactants, respectively. The gold nanoparticles began to assemble into nanocomposites within 2 min. The mixed solutions became visibly turbid,
indicating that an aggregation process had occurred. After 24 h, the solid precipitates were collected and washed extensively with hexane. The nanocomposites were then dried overnight before being subjected to transmission electron microscopy (TEM) measurements.

2.4. Measurements and characterization

1H NMR spectra were recorded on a Varian unity 300 M Hz spectrometer using CDCl3, DMSO-d6, dioxane, and d-THF as solvents. UV–visible absorption spectra were recorded in dilute THF solutions (10−4 M) on a HP G1103A spectrophotometer, and photoluminescence (PL) spectra were obtained on a Hitachi F-4500 spectrophotometer. Fourier transform infrared (FT-IR) spectra were proceeded on a Nicolet 360 FT-IR spectrometer, and photoluminescence (PL) spectra were recorded on a Nicolet 360 FT-IR spectrometer. Transmission electron microscopy (TEM) analyses were performed using a JEOL 2011 electron microscope with an acceleration voltage of 200 keV. The samples were prepared from THF solutions with a concentration of 1 wt.%, and the aggregates were precipitated on TEM sample grids (200 Cu mesh/carbon films).

3. Results and discussion

3.1. Fourier transform infrared (FTIR) spectroscopy

We used FTIR spectroscopy to confirm the presence of hydrogen bonds in two series of supramolecular nanocomposites comprising the side-chain polymers PBOT1–PBOT3 and PBT1–PBT3 complexed with the acid-modified AuSCOOH NPs. Figure S1 (Supplementary Information) provides representative FTIR spectra of the acid-modified AuSCOOH NPs, the H-acceptor polymer PBOT1, and the H-bonded nanocomposite PBOT1/AuSCOOH. Relative to the spectrum of the acid-modified AuSCOOH NPs, the signal for the O−H bonds in the spectrum of the H-bonded nanocomposite PBOT1/AuSCOOH should be weaker as a result of hydrogen bonding between the pyridyl groups of PBOT1 and the carboxylic acid units on the surface of the AuSCOOH NPs in the H-bonded nanocomposite. Because the content of carboxylic acid-modified surfactants was only 21% on the acid-modified AuSCOOH NPs, however, the O−H band of the acid-modified AuSCOOH NPs was too weak to be observed. On the other hand, the C=O stretching vibration at 1695 cm−1 for the H-bonded nanocomposite PBOT1/AuSCOOH revealed that the C=O groups were in a less-associated state than that in the acid-modified AuSCOOH NPs, with a weaker C=O stretching vibration at 1660 cm−1, suggesting the existence of H-bonds between the polymer and the NPs. Other supramolecular polymers have exhibited similar spectroscopic behavior as a result of H-bonding in their H-bonded polymer complexes [53–55].

3.2. Fluorescence quenching of copolymers induced by surface-modified Au NPs

Fig. 3 displays the results of fluorescence quenching studies of two fluorescent side-chain homopolymers PBOT1 and PBT1 with lateral MeO and Me substituents, respectively, titrated with the surface-modified NPs AuSCOOH and AuSC10 (average diameter: ca. 5–6 nm) at various concentrations in THF. In a previous study [55], we found that the fluorescence spectrum of the polymer PBOT1 in THF featured a signal for the emission of blue light at 440 nm. Relative to the polymer PBT1, the luminescent polymer PBOT1 exhibited a red-shifted PL emission at 449 nm, due to the stronger electron donating effect of its lateral MeO groups, which induced a narrower energy band gap. In Fig. 3a and b, the H-acceptor polymers PBOT1 and PBT1 exhibited dramatic decreases in their fluorescence intensities upon the addition of the AuSCOOH NPs (containing 21% carboxylic acid surfactants). It is conceivable that the fluorescence emission intensities of the nanocomposites PBOT1/AuSCOOH and PBT1/AuSCOOH decreased as a result of the H-bonded complexation of the H-acceptor pyridyl pendant units of the fluorescent polymers (PBOT1 and PBT1) with the H-donor acidic units of the surfactants on the AuSCOOH NPs (illustrated schematically in Fig. 1). In Fig. 3a, the fluorescent H-acceptor polymer PBOT1 (with lateral MeO substituents) appeared to readily undergo H-bonding with the AuSCOOH NPs (via the carboxylic acid-modified surfactants), thereby undergoing quenching due to supramolecular interactions. For the same reason, the titration of the fluorescent H-acceptor polymer PBT1 (with lateral MeO substituents) featured H-bonding interactions similar to those in the nanocomposite PBOT1/AuSCOOH, as confirmed in our TEM analyses (see below). For comparison, we titrated the fluorescent polymers PBOT1 and PBT1 with the alkyl-functionalized Au NPs AuSC10, presenting acid-free surfactant units. Again, we observed similar decreases in PL for the fluorescent polymers PBOT1 and PBT1 upon the addition of the AuSC10 NPs (Fig. 3c and d). In progressive fluorescence quenching experiments of the polymers PBOT1 and PBT1 upon increasing the concentration of AuSC10, in contrast to H-bonded nanocomposites (i.e., PBOT1/AuSCOOH and PBT1/AuSCOOH) we detected much weaker quenching behavior of the nanocomposites PBOT1/AuSC10 and PBT1/AuSC10. Because of the lack of H-bonding interactions of the AuSC10 NPs (containing the acid-free surfactant units) with the fluorescent polymers PBOT1 and PBT1, these NPs had much weaker PL quenching effects on PBOT1 and PBT1 than did the acid-modified AuSCOOH NPs.

Comparing the curves in the insets to Fig. 3a–d, the fluorescence quenching patterns for the polymers PBOT1 and PBT1 titrated with AuSCOOH (Fig. 3a and b) were much stronger than those titrated by AuSC10 (Fig. 3c and d). Therefore, the distinct quenching effects during the PL titrations of the fluorescent polymers PBOT1 and PBT1 by the different surface-modified AuSCOOH and AuSC10 NPs confirmed the presence of H-bonding interactions in the nanocomposites PBOT1/AuSCOOH and PBT1/AuSCOOH. In addition, upon addition of the surface-modified AuSCOOH and AuSC10 NPs, we observed analogous fluorescence quenching tendencies (albeit to different degrees) in the PL spectra in Figures S2 and S3 (Supplementary Information).
Information) for the fluorescent copolymers PBOT2–PBOT3 and PBT2–PBT3 (bearing various molar ratios of pyridyl groups). Nonetheless, although these nanocomposites exhibited comparable PL quenching trends, the various Stern–Volmer (SV) quenching constants ($K_{SV}$) for the diverse fluorescent polymers PBOT1–PBOT3 and PBT1–PBT3 (containing various molar ratios of pyridyl H-acceptors with lateral MeO and Me substituents) could be predicted specifically upon titration with the different NP quenchers (i.e., the surface-modified NPs AuSCOOH and AuSC10) in the following investigations of the PL quenching behavior. Hence, more comprehensible quenching details can be explored by the following investigation. Normally, the PL quenching behavior follows the SV relationship [56]:

$$I_0/I = 1 + K_{SV}[Q]$$

where $I_0$ and $I$ are the emission intensities of the fluorescent polymer (in this case, PBOT1–PBOT3 or PBT1–PBT3) in the absence and presence, respectively, of the quencher $Q$ (here, surface-modified Au NPs); $K_{SV}$ is the SV quenching constant; and $[Q]$ is the concentration of the quencher. Fig. 4 presents the SV plots of the polymers PBOT1–PBOT3 and PBT1–PBT3 in the presence of various concentrations of the carboxylic acid-modified AuSCOOH NPs and the non-acid-modified AuSC10 NPs; these data were replotted from the insets to Fig. 3a–d. We obtained the quenching constants ($K_{SV}$) of the fluorescent polymers PBOT1–PBOT3 and PBT1–PBT3, when titrated with the different NP quenchers (AuSCOOH and AuSC10) in THF, from the slopes of the plots in Fig. 4 (along with the inset slopes); Table 1 summarizes these values. Interestingly, comparing the fluorescence quenching effects of the AuSCOOH NPs on the homopolymers PBOT1 and PBT1, we find that the quenching constant of PBOT1 (lateral MeO substituents; $K_{SV} = 3.31 \times 10^5$ M$^{-1}$) was higher than that of PBT1 (lateral Me substituents; $K_{SV} = 2.50 \times 10^5$ M$^{-1}$). We suspect that, due to the more strongly electron-donating MeO groups of the conjugated pendent units of PBOT1, the pyridyl units of PBOT1 exerted a greater proton acceptor effect.
that did those of the pyridyl units in PBT1 upon complexation with AuSCOOH. Therefore, the strongest H-bonding interaction—that of AuSCOOH with PBT1 in the nanocomposite PBT1/AuSCOOH—induced the largest quenching constant in the PL titration experiments. Similarly, when titrated with the acid-modified AuSCOOH NPs, the copolymers PBT2 and PBT3 with lateral MeO substituents (but different molar ratios of pyridyl groups) also exhibited larger quenching constants ($K_{SV} = 2.67 \times 10^5$ and $2.19 \times 10^5$ M$^{-1}$, respectively) than did the copolymers PBT2 and PBT3 with lateral Me substituents ($K_{SV} = 2.17 \times 10^5$ and $1.7 \times 10^5$ M$^{-1}$, respectively). The higher quenching constants of the fluorescent copolymers PBT2 and PBT3 and of PBT2 and PBT3 relative to those of the homopolymers PBT1 and PBT1 (when titrated with AuSCOOH) might be due to their lower molar ratios of pyridyl H-acceptors, thereby affecting the homogeneous dispersion of the AuSCOOH NPs and minimizing their PL quenching effects.

On the other hand, because of the absence of H-bonding interactions when we titrated the homopolymers PBT1 and PBT1 with the non-acid-modified AuSC10 NPs (inset to Fig. 4), the quenching constants of PBOT1 and PBT1 ($K_{SV} = 2.15 \times 10^4$ and $2.30 \times 10^4$ M$^{-1}$, respectively) were both much lower than those ($K_{SV} = 3.31 \times 10^5$ and $2.50 \times 10^5$ M$^{-1}$, respectively) obtained when titrated with the carboxylic acid-modified AuSCOOH NPs (forming H-bonded nanocomposites). Surprisingly, when titrated with the non-acid-modified AuSC10 NPs, the quenching constant ($K_{SV} = 2.15 \times 10^4$ M$^{-1}$) of PBT1 was less than that ($K_{SV} = 2.30 \times 10^4$ M$^{-1}$) of PBT1. Hence, the quenching mechanisms of PBOT1 and PBT1 induced by the non-acid-modified AuSC10 NPs (in the absence of H-bonds) are different from those induced by the acid-modified AuSCOOH NPs (in the presence of H-bonds). Here, the assembly of the fluorescent polymers PBOT1 and PBT1 with the non-acid-modified AuSC10 NPs originated from dipole–dipole interactions, rather than H-bonding. Consequently, the dipole–dipole interactions of the AuSC10 NPs with PBT1 (lateral MeO groups) were stronger than those with PBT1 (lateral Me groups). As a result, the stronger binding interactions of the AuSC10 NPs with PBT1 (lateral MeO groups) induced less quenching because of the weaker association of the pyridyl conjugated structures in PBT1 with the AuSC10 NPs. Overall, the lateral MeO groups competed with the pyridyl termini of the polymer PBOT1 for interactions with the non-acid-modified AuSC10 NPs, thereby diluting the quenching effects of the AuSC10 NPs toward the polymer PBOT1 and, as a result, decreasing its value of $K_{SV}$. Accordingly, when titrated with the non-acid-modified AuSC10 NPs (inset to Fig. 4), the copolymers PBOT2 and PBT3 with lateral MeO substituents (but with different molar ratios of pyridyl groups) also exhibited smaller quenching constants ($K_{SV} = 1.82 \times 10^5$ and $1.51 \times 10^5$ M$^{-1}$, respectively) relative to those of the copolymers PBT2 and PBT3 with lateral Me substituents ($K_{SV} = 1.96 \times 10^5$ and $1.66 \times 10^5$ M$^{-1}$, respectively). We suspect that the smaller quenching constants of the fluorescent copolymers PBOT2, PBT3, PBOT2, and PBT3 relative to those of the homopolymers PBT1 and PBT1 (when titrated with AuSC10) resulted from the lower molar ratios of pyridyl H-acceptors in the former copolymers (and weaker dipole–dipole interactions with the NPs), thereby minimizing the aggregation of the AuSC10 NPs and decreasing their PL quenching effects.

Because of the absence of H-bonding interactions in the nanocomposites PBT1–PBT3/AuSC10 and PBT1–PBT3/AuSC10, all of the values of $K_{SV}$ (in Table 1) of the polymers PBT1–PBT3 and PBT1–PBT3 blended with the non-acid-modified Au NPs (AuSC10) were much (ca. 10 times) lower than those obtained when H-bonded with the

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\begin{align*}
\text{Table 1} & \\
& \text{Stern–Volmer constants ($K_{SV}$) for polymers PBOT1–PBT3 and PBT1–PBT3 titrated with different nanoparticle quenchers (AuSCOOH and AuSC10) in THF solutions.} \\
& \\
& \begin{array}{|c|c|c|c|c|c|c|}
& \hline
& \text{PBOT1} & \text{PBT1} & \text{PBOT2} & \text{PBT2} & \text{PBOT3} & \text{PBT3} \\
& \hline
& \text{AuSCOOH} & 2.50 \times 10^5 & 2.17 \times 10^5 & 1.70 \times 10^5 & 3.31 \times 10^5 & 2.67 \times 10^5 & 2.19 \times 10^5 \\
& \text{AuSC10} & 2.30 \times 10^4 & 1.96 \times 10^4 & 1.66 \times 10^4 & 2.15 \times 10^4 & 1.82 \times 10^4 & 1.51 \times 10^4 \\
& \hline
\end{array}
\end{align*}
\]

* The quenching behavior follows the Stern–Volmer relation $I_0 / I = 1 + K_{SV}[Q]$, where $I_0$ and $I$ are the emission intensities of the fluorescent polymers (PBOT1–PBT3 and PBT1–PBT3) in the absence and presence of the nanoparticle quencher $Q$ (surface-functionalized gold nanoparticles AuSCOOH and AuSC10), respectively, $K_{SV}$ is the Stern–Volmer quenching constant, and $[Q]$ is the concentration of the nanoparticle quencher.
carboxylic acid-modified Au NPs (AuSCOOH). Hence, H-bonding interactions played a very important role in determining the PL quenching effect of the fluorescent polymers induced by the Au NPs. Moreover, we have developed a multicomponent self-assembly process involving PL quenching of fluorescent polymers (such as polymers PBOT1–PBOT3 and PBT1–PBT3 with various molar ratios of pyridyl H-acceptors) titrated by different surface-modified Au NPs (AuSCOOH and AuSC10 bearing acid and acid-free surfactants, respectively), which can be utilized by other systems in the future study. On the whole, significant supramolecular interactions between various surface-modified Au NPs and fluorescent polymers can be distinguished merely by the distinct fluorescence quenching behavior with specific quenching constants (KSV). Interestingly, as the molar ratio of the pyridyl units in the fluorescent polymers decreased, the values of KSV decreased exponentially (Fig. 5), suggesting that the plots of the SV constants followed the fitable exponential equation:

\[ K_{SV} = A(1 - e^{-BX}) \]

where X is the mole percentage of pyridyl units in the fluorescent polymers and A and B are constants for the exponential curve fittings. Fig. 5 displays the fitted exponential curves and data points (acquired from the slopes of the SV plots in Fig. 4 and Table 1) of the SV constants (KSV) for the nanocomposites PBOT/AuSCOOH (A = 3.33 x 10^5, B = 3.21), PBT/AuSCOOH (A = 2.61 x 10^5, B = 3.06), PBT/AuSC10 (A = 2.33 x 10^4, B = 3.47), and PBOT/AuSC10 (A = 2.13 x 10^4, B = 3.78). Using this plot, it would be easy to predict the SV constants of fluorescent polymers containing other molar ratios of pyridyl conjugated units. Compared with the H-bonded nanocomposites PBOT/AuSCOOH and PBT/AuSCOOH, the much lower values of KSV of the polymers PBOT1–PBOT3 and PBT1–

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**Fig. 5.** Schematic curves of Stern–Volmer constants (Ksv) vs. mol% of pyridyl units (X) in fluorescent polymers (PBOT1–PBOT3 and PBT1–PBT3) as titrated by different nanoparticle quenchers (AuSCOOH and AuSC10), which follow the exponential equation (as lines) of Ksv = A[1 – exp(–BX)], where A and B are constants for the exponential curve fittings. The data points of Stern–Volmer constants (Ksv) for nanocomposites PBOT/AuSCOOH ( □ ), PBT/AuSCOOH ( ● ), PBT/AuSC10 ( ● ), and PBOT/AuSC10 ( ● ) were acquired from the slopes of Stern–Volmer plots in Fig. 4 and Table 1, and their (A and B) values for the exponential curve fittings are (A = 3.33 x 10^5, B = 3.21), (A = 2.61 x 10^5, B = 3.06), (A = 2.33 x 10^4, B = 3.47), (A = 2.13 x 10^4, B = 3.78), respectively.

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**Fig. 6.** UV–visible spectra of (a) polymer PBOT1 titrated by varying the concentration of acid-donor-modified gold nanoparticles (AuSCOOH) and (b) polymer PBT1 titrated by varying the concentration of non-acid-modified gold nanoparticles (AuSC10) in THF solutions.
PBT3, respectively, when blended with the non-acid-modified AuSC10 NPs (without H-bonding), necessitated that we enlarged the exponential curves of the values of $K_{SV}$ for the nanocomposites PBOT/AuSC10 and PBT/AuSC10 when plotted in the inset to Fig. 5.

To confirm the fluorescence quenching effects induced by the surface-modified Au NPs AuSCOOH and AuSC10 on the fluorescent polymers PBOT1–PBOT3 and PBT1–PBT3, we recorded the UV–Vis absorption spectra of polymer nanocomposites containing AuSCOOH and AuSC10 [Fig. 6 and S4 and S5 (Supplementary Information)]. We would expect the UV–Vis absorption signals to change if the aggregation of fluorescent polymers was induced upon the addition of surface-modified Au NPs; here, we used the same processing conditions as those we had used for the quenching titrations of the fluorescent polymers with the Au NPs. The absorption maxima of the polymers PBOT1 (384 nm in THF) and PBT1 (350 nm in THF) in Fig. 6a and b, titrated with AuSCOOH and AuSC10, respectively, were not red-shifted upon increasing the concentrations of the Au NPs (from 0 to 121 μM). Here, we employed relatively low concentrations (<121 μM) of the Au NPs to avoid aggregation of the fluorescent polymers and the Au NPs during the titration process; as a result, we could exclude the effects of fluorescence quenching, due to aggregation of the fluorescent polymers, upon the addition of the Au NPs. Therefore, we can attribute the fluorescence quenching as arising mainly from energy transfer from the fluorescent polymers to the Au NPs.

3.3. TEM analyses

To confirm the source of the fluorescence quenching effects on the fluorescent polymers PBOT1–PBOT3 and PBT1–PBT3 induced by the surface-modified Au NPs (AuSCOOH and AuSC10), we recorded TEM images of their polymer nanocomposites [Fig. 7 and S6 (Supplementary Information)]. These images provided further insight into the morphologies of the NP aggregates. As revealed in Fig. 7a, the carboxylic acid-functionalized Au NPs (AuSCOOH) having an average diameter of approximately 5–6 nm aggregated strongly because of the self-assembly of their H-bonded surfactant units. Next, we drop-casted (onto TEM grids) solutions of the polymer nanocomposites prepared from the polymers PBOT1–PBOT3 and PBT1–PBT3 (2 mg/mL) blended with the surface-modified Au NPs AuSCOOH and AuSC10 (0.5 mg/mL) in THF. The structural ensembles revealed in the TEM images of these polymer nanocomposites were controlled by both H-bonding and dipole–dipole interactions. The H-bonding interactions in the polymer nanocomposites PBOT1/AuSCOOH and PBT1/AuSCOOH involved the carboxylic acid units on the surface-functionalized AuSCOOH NPs coordinating with the pyridyl groups on the homopolymers PBTO1 and PBT1. Thus, as revealed in Fig. 7b and c, addition of the carboxylic acid-modified AuSCOOH NPs to the polymers PBT1 and PBT1 resulted in homogeneous distributions of the AuSCOOH NPs among the polymers, induced by the H-bonded structures in these nanocomposites. In addition, because of weaker

![Fig. 7. TEM images of surface-modified gold nanoparticles and polymer nanocomposite (a) acid-modified AuSCOOH nanoparticles, (b) nanocomposite PBOT1/AuSCOOH, (c) nanocomposite PBT1/AuSCOOH, and (d) nanocomposite PBT1/AuSC10.](image-url)
supramolecular interactions, the AuSCOOH NPs were dispersed only partially in the copolymers PBOT2, PBOT3, PBT2, and PBT3 (because of their lower molar contents of pyridyl moieties), as revealed in their respective TEM images [see Figure S6 (Supplementary Information)]. To distinguish the contributions from the acid and acid-free surfactants on the surface-modified NPs AuSCOOH and AuSC10, respectively, we also blended the polymer PBT1 with the non-acid-modified AuSC10 NPs (i.e., in the absence of H-bonds). Fig. 7d reveals clearly that the non-acid-modified AuSC10 NPs aggregated more extensively within polymer PBT1, suggesting the absence of H-bonding interactions in the nanocomposite PBT1/AuSC10. Thus, the TEM images provided evidence to explain the PL quenching behavior in the polymer nanocomposites, where a better distribution of NPs among the polymers, due to H-bonds, would result in stronger PL quenching effects on the fluorescent polymers induced by suitably surface-modified Au NPs.

4. Conclusion

We have employed two series of fluorescent side-chain polymers, PBOT1–PBOT3 and PBT1–PBT3 with lateral MeO and Me substituents, respectively, but different molar ratios of their pyridyl H-acceptor moieties, and surface-modified Au NPs bearing acid and acid-free surfactants (AuSCOOH and AuSC10, respectively) to develop distinct nanocomposites. The H-acceptor polymers PBOT1–PBOT3 and PBT1–PBT3 were quenched by the surface-modified NPs AuSCOOH and AuSC10 to different extents depending on the degrees of H-bonding and dipole–dipole interactions among the fluorescent polymers and surface-modified NPs. In contrast to the predominant dipole–dipole interactions of the nanocomposites containing the non-acid-modified AuSC10 NPs, the stronger supramolecular interactions (H-bonds) in the self-assembled nanocomposites PBOT1–PBOT3/AuSCOOH and PBT1–PBT3/AuSCOOH facilitated the dispersion of the carboxylic acid-modified AuSCOOH NPs among the H-acceptor polymers, thereby providing larger fluorescence quenching effects. Due to the strong electron-donating ability of the MeO substituents in the conjugated pendant units of PBOT1, the pyridyl units in PBOT1 exerted a stronger proton acceptor effect relative to that of the pyridyl units in PBT1 upon complexation with the AuSCOOH NPs. Therefore, upon addition of the AuSCOOH NPs, the quenching constant of the laterally MeO-substituted polymer PBOT1 was greater than that of the laterally Me-substituted polymer PBT1. After titrating with various surface-modified NPs, we measured the PL quenching constants and behaviors of the fluorescent polymers and established an exponential equation to predict the SV constants of fluorescent polymers with other molar ratios of pyridyl conjugated units. Moreover, TEM images confirmed that the dispersion of the surface-functionalized Au NPs followed the supramolecular assembly behavior of the nanocomposites between the fluorescent polymers and the surface-functionalized Au NPs that we had observed in the PL quenching experiments. Based on the fluorescence quenching and recovery of such Au nanocomposites, we believe that the ability to develop chemo- and biosensor applications will be available in the near future.

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Appendix A. Supplementary data


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H.-C. Chu et al. / European Polymer Journal 47 (2011) 2266–2276

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