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Switchable control of hydrophilicity and hydrophobicity in conjugated polymer nanoparticles by carbon dioxide

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ABSTRACT

We synthesized yellow-emissive, fluorine-based conjugated polymer to fabricate CO₂-responsive conjugated polymer nanoparticles (CPNPs). The CPNPs were functionalized with tertiary amine to have responsiveness to CO₂. The amine-functionalized CPNPs became hydrophilic by CO₂, bubbling because the bubbling led to formation of cationic ammonium ions at the side chains of the hydrophobic CPNPs. This resulted in high dispersion stability in aqueous phase even after vigorous mixing in the presence of organic phase (1-octanol). Subsequent N₂ bubbling was done to remove CO₂ present in water, leading to deprotonation of the side chains of CPNPs. The CPNPs became hydrophobic and moved to the organic phase. The CO₂-responsive property was based on the amine groups in the side chain of polymer that reversibly interacted with bicarbonate ion (HCO₃⁻), formed by dissolving CO₂ in water, generating switchable hydrophilicity and hydrophobicity.

KEYWORDS

conjugated polymer nanoparticles; fluorescence; switchable hydrophilicity

1. Introduction

CPNPs are attracting much attention in fluorescent sensing and optoelectronic devices due to their high quantum efficiency and high conductivity, bright fluorescence [1, 2]. Thus, they can be applied to various fields including biomedical technology [3] and photocatalysis [4] because of their low toxicity and cost-efficiency compared with metal nanoparticles. For the applications in the biomedical fields of CPNPs, the use of biocompatible solvents is essentials. In this regard, water is a cheap, safe, biocompatible, environmentally-friendly solvent [5]. Moreover, the use of water as a solvent can open up potential possibilities for various applications such as water splitting [6], antibacterial treatment [7], photodynamic therapy [8], and water treatment [9].

To use hydrophobic CPNPs in water, dispersion stability of CPNPs in water is highly required for the biomedical application. However, unmodified pure hydrophobic CPNPs often show aggregation in aqueous phase, in which they have moderate ionic strength or contain divalent metal ions [10]. Several investigations have shown that hydrophilic modification of the surface of polymer nanoparticles improves colloidal stability [11]. However, if the formation of CPNPs are mainly driven by hydrophobic interactions,

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hydrophilic side chains can cause considerable interference in hydrophobic assembly among polymer chains [12]. Previous reports reported that stable CPNPs were formed when low number of hydrophilic side chains were introduced. The more hydrophilic side chains were introduced, the more unstable CPNPs were formed [13]. Therefore, it is important to control the introduction of hydrophilic side chains to obtain compact and stable CPNPs.

Recently, CO_2 is known for its biocompatibility and abundancy in environment, it has been used as an external stimulus for manipulating the wettability of materials [14]. The CO_2 -responsiveness of polymers containing tertiary amines was reported by Zhao and his co-workers [14]. The pK_a of conjugated acid of tertiary amines ranges from about 6.0 to 7.0 [15]. It means that they can be easily protonated by bicarbonate anion (pH ~ 4.0-5.0), simply formed by dissolving CO_2 in water [16]. In addition, the resultant ammonium ions can be deprotonated by the removal of CO_2 . Therefore, the tertiary amines reversibly form hydrophilic ammonium salts and deprotonated amine upon addition and removal of CO_2 , respectively. Using such a property, we synthesized yellow-emissive conjugated polymer and fabricated stable CPNPs by controlling the degree of functionalization of tertiary amines as hydrophilic side chains in CPNPs. They showed high colloidal stability in water and switchable wettability by CO_2 .

2. Experimental

Instruments and materials

¹H NMR spectra were obtained from a Bruker Fourier-300 spectrometer (Korea Basic Science Institute). UV-vis absorption spectra were recorded on a PerkinElmer Lambda 35 spectrometer. Photoluminescence spectra were taken using a Varian Cary Eclipse spectrometer. The molecular weight was determined by gel-permeation chromatography (GPC), with tetrahydrofuran (THF) as an eluent with a polystyrene standard. Zeta-potentials and size distributions were measured by dynamic light scattering (DLS, Zetasizer Nano ZS, Malvern). Elemental analysis was performed with a CE Instruments EA-111- elemental analyzer. All chemicals were purchased from Sigma-Aldrich (U.S.A.) and solvents were purchased from Samchun Chemicals (Korea). All reagents were used without further purification unless otherwise noted.

Synthesis of 2,7-Dibromo-9,9-bis(6-bromohexyl)fluorene (1) [17]

2,7-Dibromofluorene (2 g, 6.17 mmol) and tert-butylammonium bromide (TBAB, 200 mg, 0.62 mmol) were dissolved in 1,6-dibromohexane (10 mL) and 50% KOH solution (20 mL) was then injected under nitrogen. The solution was stirred at 75 °C for 2 h. The reaction mixture was extracted with dichloromethane and the resulting solution was evaporated. The reaction mixture was crystallized from methanol to remove the 1,6-dibromohexane. The product was further purified by column chromatography using hexane and dichloromethane. The final product was a white solid (yield 1.96 g, 49%). ¹H NMR (300 MHz, CDCl₃, ppm) 7.51 (d, 2H, J = 8Hz), 7.45 (dd, 2H, J = 2Hz, 2Hz), 7.43 (d, 2H, J = 1.5Hz), 3.27 (t, 4H, J = 7Hz), 1.97 (m, 4H), 1.64 (m, 4H), 1.17 (m, 4H), 1.05 (m, 4H), 0.59 (m, 4H).

2.1.2. Synthesis of conjugated polymer (2) [17]

1 (650 mg, 1 mmol) and 2,1,3-benzothiadiazole-4,7-diboronic acid pinacol ester (388 mg, 1 mmol) were dissolved in dry toluene (15 mL). Tetrakistriphenylphosphine palladium(0) (59 mg, 0.05 mmol) and 2M potassium carbonate aqueous solution were added to the solution. The mixture was purged with nitrogen under stirring and heated at 85 °C for 48 h. After cooling down to room temperature, the reaction mixture was precipitated in methanol (200 mL). The obtained orange powder was purified in a Soxhlet apparatus and dried (yield 376mg, 60%).

 ^1H NMR (300 MHz, CDCl₃, ppm) : 8.06 (8H), 3.32 (4H), 2.17 (4H), 1.73 (4H), 1.3 (8H), 0.94 (4H).

Synthesis of amine-functionalized conjugated polymer (3) [18]

To a solution of **2** (100 mg) in dry THF (8 mL), diethylamine (DEA, 2 mL) was added dropwise. The mixture was purged with nitrogen and heated at 50 $^{\circ}$ C for 24 h. After the reaction, the solution was filtered to isolate ammonium bromide salt and the solvent



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Scheme 1. Synthesis of 3.

was further evaporated under reduced pressure. The product was washed in water overnight, isolated by filtration, and washed with water and methanol. The red orange powder was obtained (yield 87mg, 92%).



Figure 1. ¹H NMR spectra of (a) 2 and (b) 3 in CDCl₃.

Preparation of amine-functionalized conjugated polymer nanoparticles (CPNPs)

3 (2 mg) was dissolved in THF (20 mL). 1 mL of the solution was injected quickly into mixed solution (12 mL) of deionized water and methanol (9: 3, ν/ν) during sonication. The THF was removed by CO₂ blowing, followed by filtration through a syringe filter (0.22 μ m).

CO₂-responsiveness of CPNPs

CPNPs in water (5 mL) was added into a 20 mL vial. An equal amount of 1-octanol (5 mL) was added to the vial. Then CO_2 was bubbled to the mixture and mixed vigorously. After that, CPNPs was uniformly dispersed in aqueous phase. CO_2 was substituted by N₂, followed by vigorous mixing, resulting in CPNPs in 1-octanol phase.

3. Results and discussion

The synthetic route to the amine-functionalized conjugated polymer 3 was shown in Scheme 1. The monomer with alkyl halides (1) was synthesized according to previous report [17]. The conjugated polymer containing benzothiadiazole (2) was synthesized



Figure 2. (a) UV-vis and (b) fluorescence spectra of 2 in chloroform (■) and CPNPs in water (○).

via the Suzuki cross-coupling reaction in the presence of Pd catalyst. The number- and weight-average molecular weights of 2 were determined by GPC and found to be 6520 and 22830, respectively. The CO₂-responsive conjugated polymer 3 was obtained via modification of 2 with DEA. Elemental analysis of 3 indicated that the functionalization of amine groups was performed with 61%. Thus copolymer 3 was obtained, in which m: n was 61: 39 as mol%. In the NMR spectra of 2, the peak corresponding to the



(b)

Scheme 2. (a) Preparation of CPNPs by reprecipitation and (b) phase transfer of CPNPs by N2 bubbling.

Table 1. DLS data of CPNPs in water at 25 °C.

	Size (nm)	Zeta potential (mV)
After CO ₂ bubbling	150 ± 0.2	$+35 \pm 3$
After N ₂ bubbling	170 ± 10	$+14 \pm 2$



Figure 3. Fluorescence spectra of layers and photographs of the location of CPNPs (a) before CO_2 bubbling, (b) after CO_2 bubbling and shaking, followed by (c) N_2 bubbling and shaking. Upper and lower phases in the vial correspond to 1-octanol (oil) ($_{\odot}$) and water (\blacksquare) layers, respectively.

carbon protons adjacent to the bromine was shown at 3.3 ppm (Fig. 1a). The peak was decreased and a new peak was observed at 2.4 ppm upon the reaction of **2** with DEA (Fig. 1b). The peak of 3.3 ppm did not completely disappear after the reaction with DEA, and the degree of amination was calculated by peak integration. The peak integration of g: h were measured as 1: 2 (Figure 1b), resulting in the degree of amination was calculated to be 66%. Therefore, it was concluded that the amination was performed by about 60%.

3 exhibited UV-vis absorption at 314 nm and 444 nm (Figure 2a) and had a strong yellow fluorescence at 542 nm in chloroform solution (Figure 2b). CPNPs were prepared by conventional reprecipitation method (Scheme 2a). The UV-vis absorption and fluorescence emission of CPNPs were similar to those of **3** with slight red shift. The particle size and zeta potential of CPNPs from DLS are tabulated in Table 1. The average particle size of CPNPs after CO₂ bubbling was found to be 150 nm with zeta potential of +35 mV. A larger size and less positive zeta potential of CPNPs were obtained after N₂ bubbling. This is because of the protonation of tertiary amines by bicarbonate anions that was formed when CO₂ was dissolved in water, confirming that the CPNPs were hydrophilized after CO₂ bubbling with positive charge introduced on the surface of CPNPs. Tertiary amine is easily protonated with an aid of HCO₃⁻ ion. (below equations) [19].

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+$$
 (1)

$$R_3N + HCO_3^{-} + H^+ \leftrightarrow R_3NH^+HCO_3^{-}$$
⁽²⁾

To elucidate switchable hydrophilicity and hydrophobicity of CPNPs by CO_2 , dispersion stability was investigated on water (water)-1-octanol (organic) bilayer. After CO_2 bubbling, most CPNPs were uniformly located in aqueous phase with stable dispersion (photograph in Figure 3a), even after vigorous shaking (photograph in Figure 3b). The location of CPNPs can be verified by fluorescence spectra of CPNPs in 1-octanol and water after vigorous shaking, exhibiting higher fluorescence in aqueous phase (Figure 3b). Therefore, it was confirmed that CPNPs became hydrophilic by the presence of CO_2 and preferred locating in aqueous phase rather than in organic phase (1-octanol). N₂ bubbling and shaking was conducted to remove the CO_2 charged in aqueous phase. After the N₂ bubbling, the CPNPs dispersed in water was transferred to the 1-octanol phase, and the fluorescence in aqueous phase almost disappeared and a strong intensity of CPNPs in 1-octanol was observed (Figure 3c). This was because ammonium ions on the surface of CPNPs were deprotonated as CO_2 was substituted by N₂, so that CPNPs became hydrophobic, preferring the location in the organic phase rather than in the water phase.

4. Conclusion

We fabricated tertiary-amine functionalized conjugated polymer nanoparticles by simple reprecipitation method and investigated their CO_2 -responsive properties. After CO_2 bubbling, CPNPs became hydrophilic and uniformly dispersed in water and they stayed in aqueous phase even after vigorous mixing in a water/1-octanol bilayer. When the CO_2 dissolved in the aqueous phase was removed by N₂, CPNPs became hydrophobic and phase transfer took place, in which they moved to organic phase. Based on these

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results, switchable hydrophilicity and hydrophobicity control of CPNPs by CO_2 and N_2 was successfully elucidated. It is expected that CPNPs with enhanced dispersion stability in water can be used for various applications in water as a solvent.

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