Design and Synthesis of a New Conjugated Polyelectrolyte as a Reversible pH Sensor

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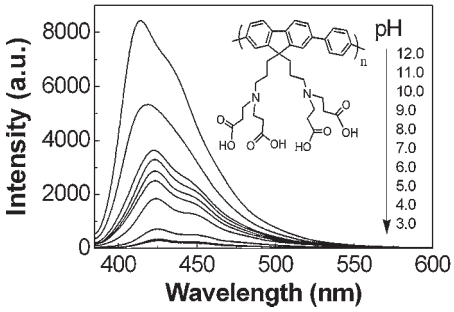
A highly pH sensitive water-soluble polyfluorene derivative (PFP-aa) has been designed and synthesized by Suzuki coupling reaction. The PFP-aa contains two amino and four carboxylic acid groups in each repeat unit (RU). The protonation and deprotonation of both the carboxylate and amine are controlled by medium pH values. The polymer charge is anticipated to control electrostatic repulsion between polymer chains and lead to different levels of aggregation behaviors. Different fluorescent responses of the PFP-aa are demonstrated as the environmental pH is changed from 3 to 12. Different sugars can bind to boronic acid to form boronic esters with different binding constants following proton release, thus generating diverse changes in pH. It is demonstrated that PFP-aa can be used as a pH sensor to detect D-fructose.



Introduction

In recent years, conjugated polymers (CPs) that serve as signal transducers in chemical and biological sensors have been paid much attention.[1–4] Relative to small molecule counterparts, their advantage is the amplification of the signal by collective optical response.[1] Solubility in aqueous media is essential for interfacing with biological substrates such as proteins and DNA, which is achieved by attaching charged functionalities (sulfonate acid, carboxylic acid, or ammonium) as pendant groups on the conjugated backbone.[5–7] Their photophysical property, aggregation, and conformation are easily perturbed by external stimuli to result in large changes in measurable optical signals. We and others have utilized this property to detect DNA, RNA, proteins, and metal ions.[8–13] Nevertheless, scarce pH sensors based on water-soluble CPs have been reported up to date.[14–16]

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pH detection in aqueous media has attracted much interest for medical, biology research, human health, and environmental protection.[17–22] The pH sensitive water-soluble CPs previously reported only respond over small pH range, typically from 4.0 to 7.0.[14,16] Hence it is necessary to design a new pH sensor based on water-soluble CPs that works over a wide pH range. To attain the goal, here we synthesize a new polyfluorene (PFP-aa) bearing a side chain that contains two amino and four carboxylic acid groups in each repeat unit (RU), which exhibits a wide pH gap for protonation and deprotonation. The pH change reversibly controls the emission of PFP-aa mediated by aggregations, thus PFP-aa can be utilized as a new and reversible pH sensor over a wide pH range from 3 to 12.

Sugars are one of the primary biological materials. In recent years, the development of fluorescent sensors for sugar detection has attracted much attention.[23] Although several intriguing strategies based on a boronic acid chelator have been developed, they require labeling of boronic acid with fluorophores or electro-active chromophores.[24–26] Development of sensors without boronic acid labeling is needed.[27] Different sugars can bind to boronic acid to form boronic esters with different binding constants following proton release, thus they generate diverse changes in pH.[27] To take advantage of this pH

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change, herein we used PFP-aa as a pH indicator to detect sugars in aqueous buffer solution.

Experimental Part

Materials and Measurements

The chemicals were purchased from Acros or Alfa Aesar, and used as received. All solvents were purified using standard procedures. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV300 or AV400 spectrometer. UV-vis spectra were taken on a JASCO V-550U spectrometer. Linear light-scattering spectra were obtained using a Hitachi F-4500 spectrofluorometer. Fluorescence measurements were obtained in 3 mL quartz cuvettes at room temperature using a Hitachi F-4500 spectrofluorometer equipped with a Xenon lamp excitation source. The excitation wavelength is 375 nm. The water was purified using a Millipore filtration system.

Synthesis of 2,7-Dibromo-9,9-bis(3′-bromopropyl)fluorene (2)

To a solution of 2,7-dibromofluorene (**1**) (5 g, 15.4 mmol) in 23 mL of 1,3-dibromopropane at 60 °C was added 50 mL of KOH aqueous solution (50%) and tetra-*n*-butyl-ammonium bromide (0.7 g). The mixture was stirred at 75 °C for 20 min and then cooled to room temperature. After extraction with CH_2Cl_2, the organic layer was washed with H_2O, 1 M HCl, and H_2O, respectively, and then dried over anhydrous $MgSO_4$. The solvent and excess 1,3-dibromopropane were removed under reduced pressure, and the residue was purified by silica gel chromatography using petroleum ether/CH_2Cl_2 (9: 1) as the eluent to afford a white solid (5.4 g, 62%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.54$ (d, 2H), 7.49 (d, 4H), 3.13 (t, 4H), 2.14 (t, 4H), 1.13 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 150.26$, 138.53, 130.54, 125.76, 121.56, 121.07, 54.07, 38.06, 33.26, 26.54.

MS (MALDI-TOF): 566.4 (M).

$C_{19}H_{18}Br_4$: Calcd. C 40.32, H 3.21; Found C 40.57, H 3.25.

Synthesis of 2,7-Dibromo-9,9-bis(3′-azidopropyl)fluorene (3)

A solution of **2** (0.5 g, 0.88mmol) and NaN_3 (0.144 g, 2.21 mmol) in 20 mL of dimethyl sulfoxide (DMSO) was stirred at 70 °C for 8 h. After cooling to room temperature, 30 mL of water was added and extracted with chloroform. The organic layer was washed with water, and then dried over anhydrous $MgSO_4$. The solvents were removed under reduced pressure and the residue was purified by silica gel column chromatography using petroleum ether/CH_2Cl_2 (9: 1) as the eluent to give a white solid (0.388 g, 90%).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.54$ (d, 2H), 7.49 (t, 4H), 3.03 (t, 4H), 2.05 (t, 4H) 0.87 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 150.28$, 138.62, 130.53, 125.64, 121.58, 121.06, 54.33, 50.86, 36.66, 22.92.

MS (MALDI-TOF): 490.5 (M).

$C_{19}H_{18}Br_2N_6$: Calcd. C 46.55, H 3.70, N 17.15; Found C 46.47, H 3.79, N 17.23.

Synthesis of 2,7-Dibromo-9,9-bis(3′-*tert*-butylcarbamate-propyl)fluorene (4)

A mixture of **3** (0.6 g, 1.22 mmol), 22 mL of tetrahydrofuran (THF), 3 mL of H_2O, and PPh_3 (0.80g, 3.06 mmol) was stirred at room temperature for 12 h. After removing the solvents, the residue was dried under vacuum. The residue and di-*tert*-butyl dicarbonate (0.588 g, 2.69 mmol) were then dissolved in 25 mL of THF, and the solution was stirred under room temperature for 12 h. The solvents were removed under reduced pressure and the residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3: 1) to afford a white solid (0.67 g, 86%).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.52$ (d, 2H), 7.47 (d, 2H), 7.43 (s, 2H), 4.27 (br, 2H), 2.89 (t, 4H), 1.97 (t, 4H), 1.40 (s, 18H), 0.75 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.34$, 150.87, 138.58, 130.25, 125.62, 121.4, 120.90, 78.69, 54.47, 39.95, 36.73, 27.94, 24.07.

MS (MALDI-TOF): 677.6 [M + K].

$C_{29}H_{38}Br_2N_2O_4$: C 54.56, H 6.00, N 4.39; Found C 54.55, H 6.08, N 4.37.

Synthesis of Monomer (5)

HCI (37%, aqueous, 1.5 mL), 8 mL of H_2O, **4** (0.3 g, 0.47 mmol), and 16 mL of 1,4-dioxane were added to a 50 mL round-bottom flask. The mixture was stirred at 50 °C for 16 h. After cooling to room temperature, the solvents were removed under reduced pressure and the residue was dissolved in 5 mL of methanol. A solution of KOH (0.7 g) in 2 mL of water was then added. The methanol was removed and the residue was extracted with CH_2Cl_2. The organic layer was washed with water, and then dried over anhydrous $MgSO_4$. The solvent was removed and the residue was dissolved in 10 mL of methanol. To this solution, 0.175 mL of methyl acrylate and boric acid (2.45 mg) in 0.4 mL of water were added. The mixture was stirred at room temperature for 12 h. The solvents and the excess methyl acrylate were removed, and the residue was extracted with CH_2Cl_2. The organic layer was washed with water and dried over anhydrous $MgSO_4$. After removing CH_2Cl_2, the residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1: 1) as eluent to yield a colorless oil (0.23 g, 62%).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.52$ (d, 2H), 7.47 (t, 4H), 3.63 (s, 12H), 2.55 (t, 8H), 2.30 (t, 8H), 2.15 (t, 4H), 1.94 (t, 4H), 0.71 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 172.46$, 151.57, 138.59, 129.96, 125.82, 121.19, 120.81, 54.79, 53.16, 51.08, 48.48, 36.94, 31.78, 29.24, 21.03.

MS (MALDI-TOF): 783.5 (M).

$C_{35}H_{46}Br_2N_2O_8$: Calcd. C 53.72, H 5.93, N 3.58; Found C 53.48, H 5.94, N 3.30.

Synthesis of Polymer (PFP-aa)

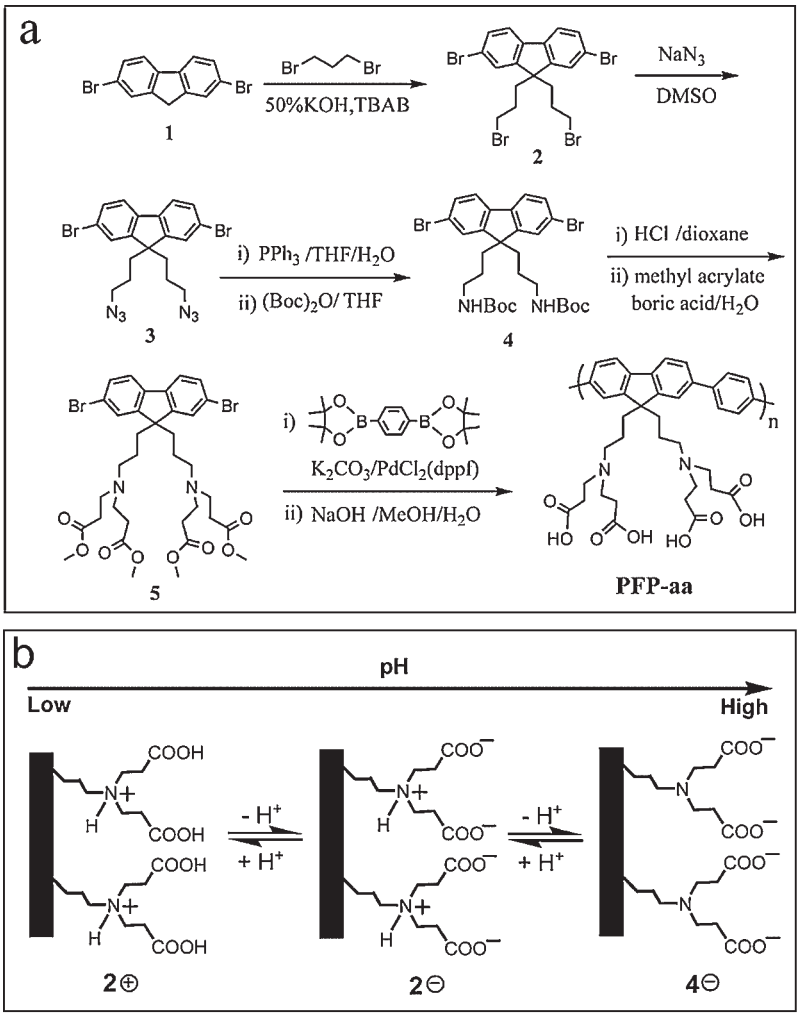
A mixture of **5** (0.13 g, 0.17 mmol), 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (55 mg, 0.17 mmol), $PdCl_2$ (dppf),

2 mL of THF, and 2 mL of 2.0 M K_2CO_3 was stirred at 90 °C for three days. After removing the solvents, methanol was added. The organic solution was poured into acetone to obtain a precipitate. The precipitate was redissolved in methanol and a solution of NaOH (0.3 g) in 3 mL of water was added. The mixture was stirred at 50 °C for 12 h. After cooling to room temperature, the methanol was removed, and the pH of the mixture was adjusted to between 8 and 9 with hydrochloride. The mixture was dialyzed against water using a membrane with a molecular weight cut-off of 7 000. The aqueous solution was then adjusted to pH 4, and the polymer was obtained by centrifugation (0.0567 g).

^{1}H NMR (300 MHz, CD_3OD/K_2CO_3: $\delta = 7.75$ (br, 7H), 7.65 (br, 3H), 7.37 (br, 1H), 7.28 (br, 1H), 2.70 (br, 1H), 2.49 (br, 8H), 2.11 (br, 15H), 0.90 (br, 4H).

The Sugar Assays

To a 3 mL quartz cuvette was added PFP-aa (5×10^{-6} M in RU) and boronic acid (25×10^{-3} M) in 2 mL of phosphate buffer solution (2×10^{-3} M, pH 9), and then sugar (25×10^{-3} M) was added into the solution. After the sample was incubated for 0.5 min, the fluorescence spectra were measured at room temperature with an excitation wavelength of 375 nm.



Scheme 1. a) Synthetic scheme for the preparation of PFP-aa. b) The charge changes per repeat unit of PFP-aa upon varying pH.

Results and Discussion

The synthetic approach to PFP-aa is outlined in Scheme 1a. Reaction of 2,7-dibromofluorene (**1**) with 1,3-dibromopropane yields 2,7-dibromo-9,9-bis(3′-bromopropyl)fluorene (**2**) followed by reaction with sodium azide in DMSO provides 2,7-dibromo-9,9-bis(3′-azidopropyl)fluorene (**3**) in 90% yield. Reduction by using PPh_3 and subsequent amine protection with di-*tert*-butyldicarbonate (Boc_2O) yields 2,7-dibromo-9,9-bis(3′-*tert*-butoxycarbonylamino-propyl)-fluorene (**4**) in 86% yield. Treatment of **4** with 1.9 M HCl in dioxane to remove Boc groups followed by Michael addition with methyl acrylate affords monomer **5**. Suzuki cross-coupling of **5** with 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene using $PdCl_2$(dppf) as catalyst in a 2.0 M potassium carbonate aqueous solution following the hydrolysis of the ester with NaOH in CH_3OH/H_2O gives crude water-soluble polymer. The polymer was dialyzed against water using a membrane with a molecular weight cut-off of 7 000 to afford PFP-aa. The polymer emits bright blue fluorescence in water (pH 7.0) and shows emission spectra with a λ_{max} at about 423 nm and a shoulder at 450 nm, which is characteristic of polyfluorenes.[11]

There are two amino and four carboxylic acid groups in one RU of PFP-aa. As shown in Scheme 1b, at low pH (pH < 3), both the carboxylate and amine are protonated, thus PFP-aa exhibits two positive charges per RU. At higher pH (pH > 5), the carboxylic acids are all deprotonated and PFP-aa exhibits two negative charges. At even higher pH (pH > 10), both the carboxylates and amines are deprotonated, thus PFP-aa exhibits four negative charges per RU.[28] Therefore, the overall negative or positive charges of the polymer vary as pH changes over a wide range. The polymer charge was anticipated to control electrostatic repulsion between polymer chains and lead to different levels of aggregation and energy transfer behaviors.[5,14] As the pH increases, the cationic conjugated polymers showed tight aggregation in aqueous solution,

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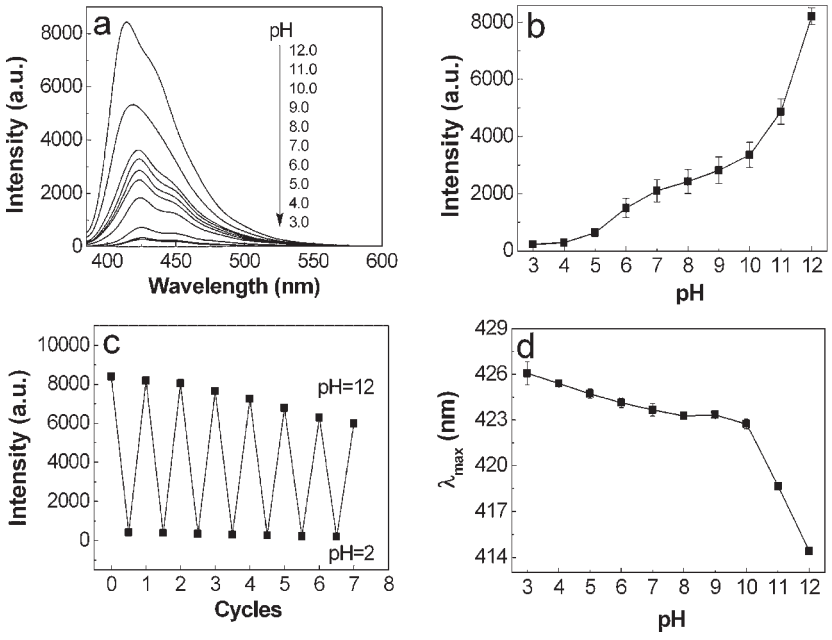

Figure 1. a) Emission spectra and b) maximum fluorescence intensity of PFP-aa as a function of pH values in water. c) The maximum fluorescence intensity of PFP-aa upon cycling the pH between 12 and 2 in water. d) Maximum wavelength of PFP-aa emission as a function of pH in water. [PFP-aa] = 5×10^{-6} M in RUs, the excitation wavelength is 375 nm. Error bars represent the deviation of three experiments.

which leads to fluorescence quenching,[29] while the anionic ones react the opposite way.[5,14] Thus, different fluorescent responses of PFP-aa are expected as the environmental pH changes.

Figure 1a shows the emission spectra of PFP-aa in water as a function of pH. The pH value of the solution ([PFP-aa] = 5×10^{-6} M in RU) was adjusted with NaOH or HCl. The intensity of the emission decreases as the pH decreases from 12 to 3.0, and then it remains unchanged for pH's lower than 3 (Figure 1b). These results show that the emission spectra of PFP-aa show highly pH-responsive characteristics over a wide pH range as expected. The pH-responsive fluorescence is reversible as the pH cycles. As shown in Figure 1c, the emission intensity can recover well at the beginning and cycles between pH 12 and 2. The attenuation of emission intensity after several cycles may be a result of the adsorption of PFP-aa to the cuvette surface. The maximum emission wavelength red shifts from 415 to 426 nm as the pH is reduced from 12 to 3.0. This is consistent with the interchain π–π stacking caused by the formation of aggregates at low pH, while the aggregation results in the self-quenching of PFP-aa. The fluorescence quantum yield of PFP-aa is 22% at pH 12 and reduces to 2.3% at pH 3. The maximum emission intensity between pH 12 and 3 is distinguishable, thus the sensor is workable over a wide range.

To test the robustness of PFP-aa as a pH sensor, the effects of interfering nicotinamide adenine dinucleotide (NADH) and fluorescence quencher (Fe^{3+} ions) that are commonly present in biological and environmental samples were studied. As shown in Figure 2, the NADH showed very minor interference on the optical response of PFP-aa. In the presence of Fe^{3+} ions, the fluorescence of PFP-aa was quenched by 35%, however, the PFP-aa still exhibited significant optical response over the pH range from 3 to 12. The minor interference from other substances clearly shows that PFP-aa can be used as a robust pH sensor over a wide pH range.

The pH-dependent aggregation of PFP-aa is also supported by absorption and scattering spectra. Figure 3a shows the absorption spectra of PFP-aa in water with varying pH. The absorption maximum is observed to red shift from 370 to 383 nm as the pH reduces from 12 to 3. At low pH, protonation of the carboxylic groups would make the PFP-aa charge positive, which leads to the red-shift of the absorption maximum because of interchain π–π interactions.[29,30] Upon increasing the pH of the aqueous polymer solution, the aggregates are broken. Reduced interchain contacts lead to reduced interchain π–π interactions following a blue shift of the absorption maximum. The emission intensity of PFP-aa at certain pH showed a minor change (approximate 5%) with

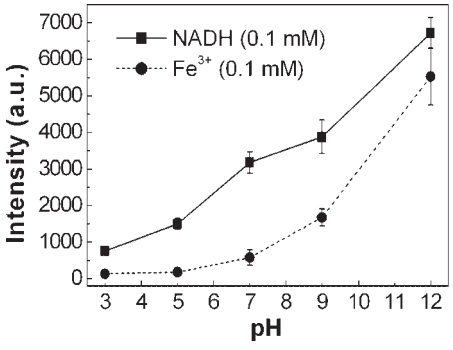

Figure 2. Maximum fluorescence intensity of PFP-aa as a function of pH values in water in the presence of NADH and Fe^{3+} ions. [PFP-aa] = 5×10^{-6} M in RUs, [NADH] = [Fe^{3+}] = 0.1×10^{-3} M. The excitation wavelength is 375 nm. Error bars represent the deviation of three experiments.

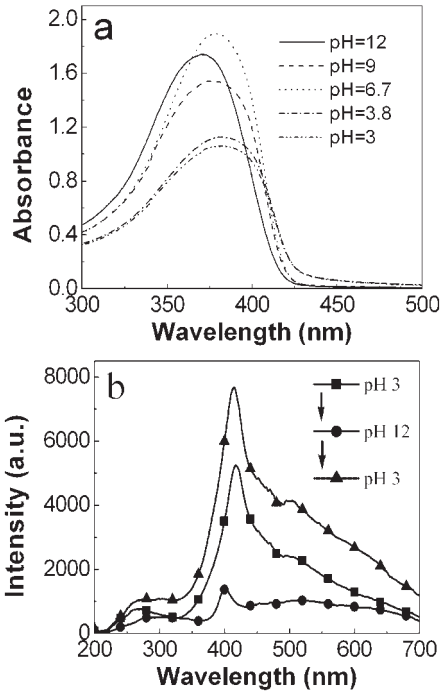

Figure 3. a) Absorption spectra of PFP-aa ([RU] = 5×10^{-5} M) in water at different pH. [PFP-aa] = 5×10^{-5} M in RUs. b) Linear scattering spectra of PFP-aa in water at pH 12 and 3. [PFP-aa] = 5×10^{-6} M in RUs, the excitation wavelength is 375 nm.

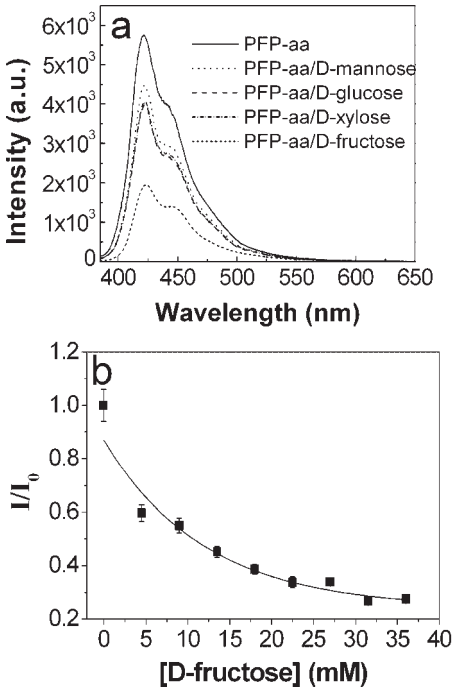

Figure 4. a) Emission spectra of PFP-aa (5×10^{-6} M in RU) in phosphate buffer solution (2×10^{-3} M, pH 9) that contains boronic acid (25×10^{-3} M) with four different sugars (25×10^{-3} M). b) Calibration plot of the D-fructose assay. [PFP-aa] = 5×10^{-6} M in RUs, [boronic acid] = 25×10^{-3} M, [D-fructose] = 0–36×10^{-3} M. The excitation wavelength is 375 nm. Error bars represent the deviation of three experiments.

excitation wavelength at 375 nm in comparison to that with absorption maxima as excitation, which excludes that changes in emission intensity as a function of pH are a result of changes in the absorption maxima. As shown in Figure 3b, the linear light scattering intensity of PFP-aa at pH 3 is five times higher than that at pH 12, which suggests that the aggregates have a big particle size in solution at low pH.[14] These results are consistent with those of fluorescence and absorption measurements. It was noted that the scattering intensity can recover well after one cycle between pH 3 and 12, which provides evidence of aggregation/de-aggregation of the PFP-aa.

Boronic acid is a weak Lewis acid ($pK_a = 9.2$) which is more basic than boronic ester ($pK_a = 3$).[27] Thus sugars bind to boronic acid to form boronic esters and generate a decrease in pH. Upon adding sugars to an aqueous solution that contains PFP-aa and boronic acid, the fluorescence of PFP-aa will be quenched. Different sugars can bind to boronic acid with different binding constants followed by proton release, thus they generate diverse changes in pH. Figure 4a shows the fluorescence spectra of PFP-aa (5×10^{-6} M in RU) in phosphate buffer solution (2×10^{-3} M, pH 9) that contained boronic acid (25×10^{-3} M) upon addition of four different sugars (each 25×10^{-3} M). For D-fructose, the fluorescence of PFP-aa is quenched by 66%, while for D-mannose, D-glucose, and D-xylose, 20, 25, and 24% fluorescence is quenched, respectively. These results are consistent with the fact that D-fructose has a larger binding constant to boronic acid than the other three sugars.[13,27] Therefore, PFP-aa can be used to selectively detect D-fructose. Figure 4b shows the titration curve against D-fructose for the PFP-aa (5×10^{-6} M in RU)/boronic acid (25×10^{-3} M) system measured in phosphate buffer solution (2×10^{-3} M, pH 9). D-Fructose can be detected in a concentration range of 0 to 36×10^{-3} M, with a detection limit of 2.0×10^{-3} M.

Conclusion

In summary, a new and reversible pH sensor has been synthesized on the basis of a water-soluble conjugated polymer. The pH change reversibly controls the emission of the conjugated polymer mediated by aggregation. Different fluorescent responses of the PFP-aa were demonstrated as the environmental pH changed from 3 to 12. It is demonstrated that PFP-aa can be used as a pH sensor to detect D-fructose.

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