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An iodide sensory property of a strongly blue-fluorescent polycationic molecular wire from a new polybenzimidazole

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Summary

A new strongly blue-fluorescent polybenzimidazole of PFBI having a fluorene group in the main chain is synthesized and characterized. A polycationic molecular wire prepared from PFBI in an acidic solvent shows the applicability for an iodide sensor.

Introduction

Due to the extended π-conjugation in the main chain of conjugated polymers, they exhibit unique electrical and optical properties such as electrical conductivity, luminescence, photoconductivity and nonlinear optical properties. And also the extended π-conjugation provides conjugated polymer-based chemical sensors with the signal amplification characteristics, which is their major merit over sensors based on small molecules [1].

Almost all chemosensors based on conjugated polymers have been designed to have electron-donating groups such as crown ethers, aza crown ethers, calixarenes and nitrogen-containing heterocycles for recognition of cation analytes such as proton and metal ions [1]. On the other hand, anion sensors are one of the major objectives in supramolecular chemistry [2]. In the field of conjugated polymer sensors, however, anion recognition and sensing systems have rarely been reported. Tour's group reported the zwitterionic pyrrole-derived polymers and protonated imine-bridged poly(pyridinethiophene)s exhibit the sensing ability for halides [3,4]. More recently, boronic acid or boronate-substitued polythiophenes have been reported sensitive to a fluoride ion[5]. On the other hand, in supramolecular chemistry, positively charged hosts having aliphatic or aromatic polyammonium, guanidinium or imidazole groups have been designed for sensing anion guests [2].

In this study, we describe the synthesis, characterization and anion-sensing property of a new polybenzimidazole having a fluorene group (Poly(9,9-dihexylfluorene-2,5-diyl-*alt*-5,5'-bibenzimidazole), PFBI).

Experimental

Instruments

Melting points were measured on an Electrothermal IA9100 digital melting point apparatus. ^{1}H and ^{13}C NMR and IR spectra were obtained using a Varian VXR-300 FT-NMR spectroscopy and a Nicolet 360 FT-IR spectroscopy, respectively. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were conducted with a TA instruments SDT 2960 unit and a TA instruments DSC 2010 unit, respectively, at a heating rate of 10 °C/min under a N_2 atmosphere. UV-visible absorption and fluorescence spectra were recorded on a Shimadzu UV-2101PC UV-visible scanning spectrophotometer and a Shimadzu RF 5301PC Spectrofluorophotometer, respectively. Fluorescence quantum efficiencies were calculated with 9,10-diphenylanthracene in cyclohexane as a reference using the equation (1) as folloews :

$$\Phi_{\mathrm{PL},s} = \Phi_{\mathrm{PL},r}\cdot(A_r/A_s)\cdot(F_s/F_r)\cdot(n_s/n_r)^2 \qquad \textbf{(1)}$$

where Φ_{PL}, A, F and n are the fluorescence quantum efficiency, the absorbance at the excitation wavelength, the integral over the fluorescence spectrum and the refractive index of the solvent, respectively and the subscripts of s and r refer to the sample and the reference solution specimens, respectively [6].

Synthesis of 2,7-dibromo-9,9-dihexylfluorene (1)

2,7-Dibromofluorene (20.00 g, 62 mmol), KOH (20.46 g, 310 mmol) and KI (4.98 g, 30 mmol) were stirred in DMSO (42 mL) in a water-cooling bath for 3 h under N_2. 1-Bromohexane (31.33 g, 186 mmol) was added to the dark reddish mixture. The reaction mixture was stirred for 20 h under N_2 and then diluted with water (300 mL) and ethanol (50 mL). The crystalline product was filtered off and washed with ethanol and water. Recryatallization from hexane provided the pure colorless product. Yield 27.58 g (91 %); mp 67 - 68 °C; IR (KBr, cm^{-1}): 3067 (aromatic C–H), 2922 and 2853 (aliphatic C–H) and 1058 (C–Br); ^{1}H NMR ($CDCl_3$, ppm): δ 7.51 (2 H), 7.46 (2 H), 7.44 (2 H), 1.91 (4 H), 1.05 (12 H), 0.77 (4 H), 0.58 (6 H); ^{13}C NMR ($CDCl_3$, ppm): δ 152.5, 139.0, 130.1, 126.1, 121.4, 121.1, 55.6, 40.2, 31.4, 29.5 (br), 23.6, 22.6, 14.0.

Synthesis of 2,7-dicyano-9,9-dihexylfluorene (2)

The mixture of (**1**) (16.38 g, 33 mmol) and CuCN (9.03 g, 100 mmol) in dry DMF (100 mL) was refluxed for 8 h under N_2. After cooling to 80 °C, the solution of $FeCl_3\cdot6H_2O$ (40.00 g) and conc. HCl (50 mL) in water (50 mL) was added to the reacted mixture. The solution was stirred at 70 ~ 80 °C for 1 h and then overnight at room temperature. The light brown precipitate was filtered off, washed with water and methanol, dissolved in chloroform and filtered through a short silica gel column. Pure pale yellow crystalline (**2**) was obtained by the removal of chloroform *in vacuo* and recryatallization from ethanol. Yield 11.98 g (94 %); mp 115 °C; IR (KBr, cm^{-1}): 3053 (aromatic C–H), 2924 and 2853 (aliphatic C–H), 2225 (C≡N); ^{1}H NMR ($CDCl_3$, ppm): δ 7.84 (2 H), 7.70 (2 H), 7.66 (2 H), 2.00 (4 H), 1.04 (12 H), 0.78 (4 H), 0.52 (6 H); ^{13}C NMR ($CDCl_3$, ppm): δ 152.0, 143.4, 131.5, 126.7, 121.4, 119.2, 111.8, 56.0, 39.8, 31.3, 29.3 (br), 23.6, 22.4, 13.9.

Synthesis of 9,9-dihexylfluorene-2,7-dicarboxylic acid (3)

(**2**) (3.85 g, 10 mmol) and KOH (7.92 g, 120 mmol) were stirred and refluxed in a triethylene glycol/water mixture (80 mL / 10 mL) for 20 h. The solution was filtered to remove insoluble parts after heating and then cooled to room temperature. The viscous filtrate was cooled to 0 °C and acidified with excess conc. HCl to pH $\cong$ 2. White precipitate was filtered off, washed with water and dried at 80 °C *in vacuo*. The pure product was obtained after recrystallization from aqueous methanol. Yield 4.08 g (96 %); IR (KBr, cm^{-1}): 2400–3600 (O–H), 2926 and 2856 (aliphatic C–H), 1682 (C=O); ^{1}H NMR (DMSO-d_6, ppm): δ 13.06 (2 H), 8.03 (6 H), 2.08 (4 H), 0.97 (12 H), 0.70 (4 H), 0.43 (6 H); ^{13}C NMR (DMSO-d_6, ppm): δ 168.2, 152.0, 144.5, 131.1, 129.5, 124.6, 121.5, 55.7, 31.5, 29.5, 24.0, 22.6, 14.4.

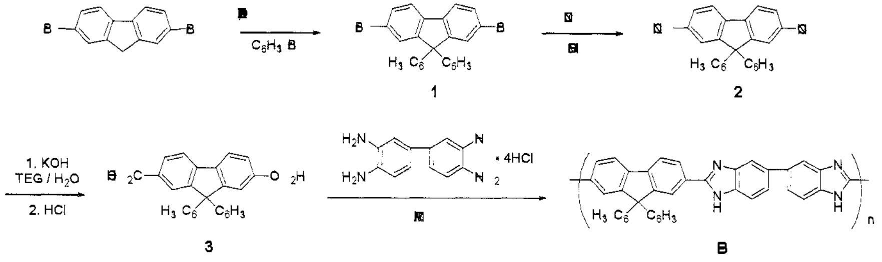
Polymerization of poly(9,9-dihexylfluorene-2,5-diyl-alt-5,5'-bibenzimidazole) (**PFBI**)

3,3'-Diaminobenzidine tetrahydrochloride (0.18 g, 0.5 mmol) was dehydrochlorinated in PPMA (5 mL) under a dry nitrogen flux at 110 °C for 2h. Dicarboxylic acid monomer **3** (0.21 g, 0.5 mmol) was added and the mixture was heated to 130 °C for 3 h while stirring under a positive N_2 flow. The resultant viscous solution was poured into a diluted NaOH solution, filtered off, washed with water and methanol several times and dried at 80 °C *in vacuo*. Twice precipitation from a formic acid solution into methanol/triethylamine was carried out for further purification. Yield 0.27 g (98 %); IR (KBr, cm^{-1}): 3500-3000 (broad, N–H in imidazole), 2919 and 2850 (aliphatic C–H), 1616 (C=N in imidazole); ^{1}H NMR (DCO_2H, ppm): δ 8.08–8.60 (12 H), 2.42 (4 H), 1.14 (16 H), 0.78 (6 H); ^{13}C NMR (DCO_2H, ppm): δ 154.5, 151.3, 145.9, 140.1, 133.0, 132.1, 128.7, 128.0, 123.7, 122.9, 115.6, 113.5, 57.4, 40.3, 31.8, 29.9, 24.5, 22.8, 14.0.

Results and Discussion

As shown in Scheme 1, **PFBI** is simply prepared from 9,9-dihexylfluorene-2,7-dicarboxylic acid and 3,3'-diaminobenzidine tetrahydrochloride *via* conventional direct condensation in phosphorus pentoxide/methanesulfonic acid (PPMA) known as the Eaton's reagent as both a condensation agent and a polymerization solvent [7,8].

The IR spectrum of **PFBI** exhibits characteristic imidazole absorption bands at 3500-3000 cm^{-1} and 1616 cm^{-1} corresponding to N-H and C=N stretching, respectively, which shows polymerization is carried out successfully[7,8]. Greenish brown fibrous **PFBI** shows poor solubility in common organic solvents except for polar aprotic solvents such as *N*-methylpyrrolidinone (NMP), *N,N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO). **PFBI** is more soluble in NMP and DMF than in DMSO. The polymer is also soluble in formic acid (98% and 85%), concentrated sulfuric acid, methanesulfonic acid and trifluoroacetic acid. Among these acidic solvents, formic acid shows best solubility.



Scheme 1. Synthetic scheme of **PFBI**.

Inherent viscosities of **PFBI** are 0.71 dL/g and 0.86 dL/g in NMP and formic acid (85%), respectively, which indicates that **PFBI** has fairly high molecular weight and, in formic acid, is protonated to have the positive charge electrostatically in the main chain.

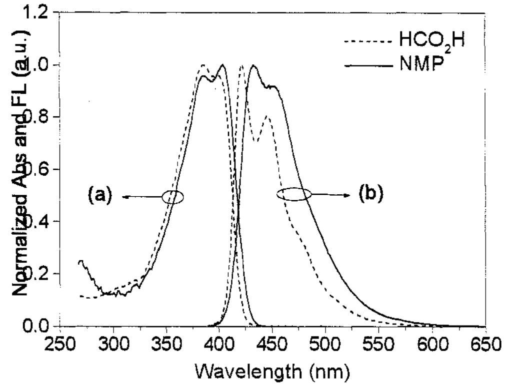
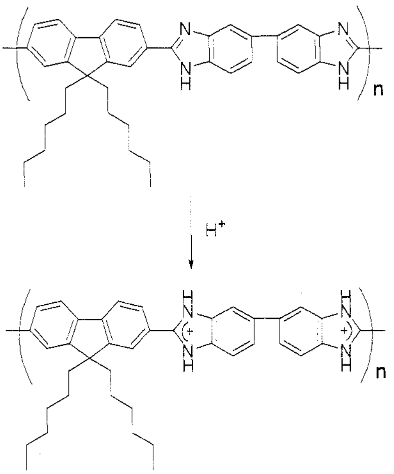


Figure 1. Abs (a) and FL (b) spectra of **PFBI** in different media (1×10^{-5} M).

As shown in Figure 1, **PFBI** shows symmetrical UV-visible absorption (Abs) and fluorescence (FL) spectra with fine vibrational structures in solution. Abs and FL spectra of the polymer in a formic acid (98%) solution exhibit blue-shift relative to that in a NMP solution. In formic acid, an imine nitrogen atom in an imidazole group is protonated and, as a result, the positive charge is introduced into the benzimidazole ring that shortens the π-conjugation length (Scheme 2). Estimated by comparison with 9,10-diphenylanthracene (FL quantum efficiency of 0.90 in cyclohexane, excitation at 350 nm), the FL quantum efficiencies of **PFBI** are 1.00 and 0.86 in NMP and formic acid (98 %), respectively. Thin, transparent and robust films of **PFBI** are readily prepared from a formic acid solution by spin-casting. However, a film exhibits weak FL with the maximum at 469 nm due to intermolecular hydrogen bonding and chain aggregation [9].



Scheme 2. Protonation of **PFBI** in an acidic solvent.

The protonation of the polymer in an acidic solvent is further investigated by the ^{1}H NMR analysis (Figure 2). The complicated aromatic proton peaks of **PFBI** are shown in 7.57–8.46 ppm in a DMSO-d_6 solution. The weak and broad peak corresponding to N-H in a benzimidazole group appears at 13.07 ppm. On the other hand, in a formic-*d* acid or a trifluoroacetic acid-*d* solution, the simplified pattern of the aromatic proton peaks appear in the downfield region relative to DMSO-d_6 due to the symmetry structure and the electron-deficiency of protonated benzimidazole groups [10,11].

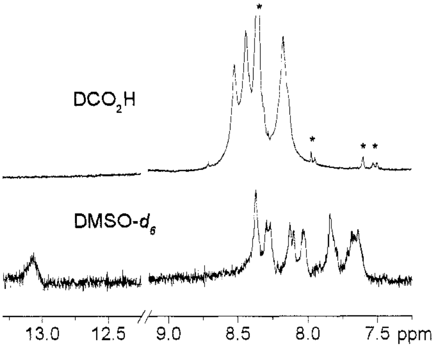


Figure 2. ^{1}H NMR spectra of **PFBI** in different media. * indicates solvent impurities.

In gemeral, polybenzimidazole complexes with acids have been studied as proton-conducting polymer electrolytes for polymer electrolyte fuel cells [12,13]. To our knowledge, chemical sensors using polybenzimidazoles have been rarely reported. This communication is the first report about the anion sensor applicability of polybenzimidazoles. Protonated **PFBI** in an acidic solvent forms a 'polycationic molecular wire', which can be applied to an anion sensor system with an electrostatical interaction mode [2]. We investigate the sensitivity of a **PFBI**/formic acid system as a fluorescence mode sensor to halides (F^-, Cl^-, Br^- and I^-). As shown in Figure 3, the fluorescence intensity of the polymer decreases on the addition of iodide without a large change of the spectrum shape. This sensor shows remarkable sensitivity to I$^-$, whereas it shows no sensitivity to F$^-$, Cl$^-$ and Br$^-$ (Figure 4). Tour's group reported that iodide exhibits high nucleophilicity over other halides in polar protic solvents [3]. So the electrophilic system of the **PFBI**/formic acid exhibits specific sensitivity to iodide with enhanced nucleophilicity.

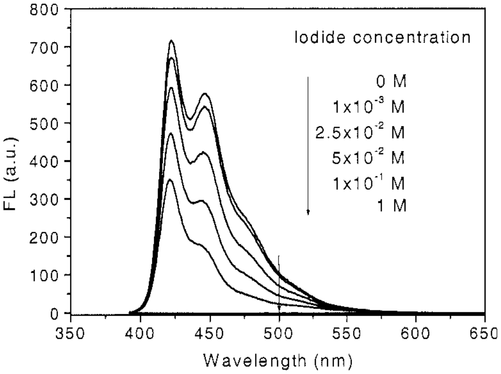


Figure 3. FL spectra changes of **PFBI** in formic acid (1×10^{-5} M) upon the addition of iodide.

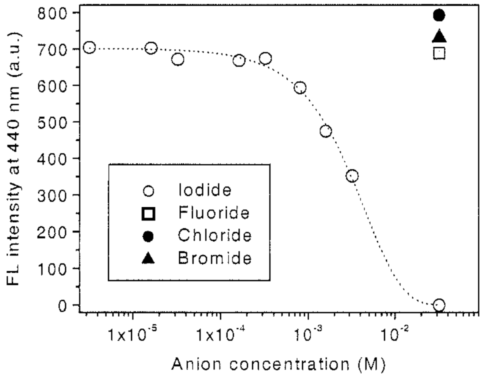


Figure 4. FL intensity changes of **PFBI** in formic acid (1×10^{-5} M) upon the addition of various anions.

Conclusions

In conclusion, a new polybenzimidazole based on fluorene, **PFBI**, is successfully synthesized. It shows blue fluorescence at 433 nm and 422 nm in NMP and formic acid, respectively, and very high fluorescence quantum efficiencies in both solutions. In a formic acid solution, **PFBI** forms a polycationic molecular wire, of which the system shows iodide sensitivity.

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