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Alternating copolymers containing fluorene and oxadiazole derivatives for fluorescent chemosensors

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1. Introduction

Several heavy metals are hazardous to health or to the environment, therefore the development of sensors displaying both sensitivity and selectivity has been dramatically raised up in recent years [1]. The facile detection and sensitivity of portable sensors are inherently more desirable than performing numerous complex analytical methods such as flame photometry, atomic absorption spectrometry, ion sensitive electrodes and electron microprobe analysis that require sophisticated instruments and are time-consuming. Conjugated polymers have emerged as one of the most promising classes of sensor materials in recent years due to their high sensitivity and selectivity, which enables for detection of a variety of analytes ranging from ions to explosives [2]. Compared to small organic compounds, polymer based chemosensors have numerous advantages such as their simplicity of use, signal amplification, easy device fabrication and a combination of different outputs [3]. Swager [4] demonstrated that conjugated polymer sensors with the receptors connected in conjugation with each other show several advantages over small molecules for sensing applications. Under photon irradiation, the sensor molecule is promoted to an excited state and the resulting exciton can rapidly migrate along the conjugated polymer backbone to a low energy acceptor site, the emission intensity

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ABSTRACT

The novel alternating copolymers containing 9,9-dioctylfluorene and *meta*-phenylene linked 2-pyridyl-1,3,4-oxadiazole or 2-pyrimidyl-1,3,4-oxadiazole were synthesized through a palladium catalyzed cross coupling reaction. The thermal and optical properties of the polymers were substantially affected by the heteroaryl substituted oxadiazole units. The absorption spectra of the copolymers in the solid state exhibited a bathochromic shift when compared to those in solution. Fluorescence quenching as examined using a fluorescence spectrophotometer was found to be directly related to concentration of the metal ions. Due to the photoinduced electron transfer mechanism, both polymer solutions act as a turn-off fluorescent chemosensor. The sensing behavior to various metal ions such as Ni²⁺, Cu²⁺, Zn²⁺ and Hg²⁺ ions revel that the polymers were highly sensitive to both Ni²⁺ and Cu²⁺ ions. The results clearly demonstrate that the copolymers can act as a potential sensory material for the detection of metal ions.

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of conjugated polymers dramatically decreases as a turn-off sensor. The other type of conjugated polymer sensor is based on the fluorescence changes in response to the conformation of the polymer backbone which was reported by Wasielewski and Wang [5]. A bipyridyl group with a dihedral angle of 20° between the two pyridine planes in the 2,2-bipyridine system was introduced into the polymer backbone. It was forced into a planar configuration after chelation to metal ions. This resulted in an increase of the conjugation length of the polymer which can be monitored by the fluorescence and absorption spectroscopy. Another approach is utilizing a conjugated polymer backbone with pendants and the concept of a polyreceptor which was demonstrated by Swager's group [6]. They attached a cyclophane-based receptor onto a poly(para-phenylene-enthynylene) backbone. Upon addition of viologen, a decrease in the fluorescence was observed as well as a 65-fold increase in the selectivity when compared to a small molecule receptor. It should be noted that the receptors are placed at a *para* position relative to the phenylene ring of the polymer chain which allows an electronic resonance interaction between the receptor and conjugated polymer backbone.

Recently, fluorene derived polymers furnished with bipyridine units have been shown to exhibit fluorescence quenching of polymer solutions by the addition of transition metal ions [7]. The influence of the polymer main chain rigidity in metal cation sensing has also been reported. Fluorene and 2,2-bipyridyl containing polymers displayed fluorescence quenching and variations in the UV-vis absorption spectra upon interaction with a wide set of transition metal ions [8]. The higher backbone flexibility of the



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polymer provided the weakest resistance to coplanarity of the two pyridine rings during chelation with metal ions, giving rise to the higher selectivity. 1,3,4-Oxadiazoles have attracted attention due to their unique optical properties and are currently exploited as signaling components in sensory systems [9]. Photoemissive 2,5diaryl-1,3,4-oxadiazoles have found wide-spread applications as electronic and photonic materials [10] and their application as the signaling component in molecular sensory systems have recently been described. There are a variety of examples of analyte binding from oxadiazole-based fluorescent chemosensors such as fluoride sensing [11], explosive nitroaromatics sensing [12] and metal ion sensing systems [13]. This structural framework allows a bidentate metal-chelating environment to be established when a metal binding site is incorporated into the 5-aryl ring. As the O and N atoms in the 1,3,4-oxadiazole moiety can be combined with this additional binding site, two options of bidentate chelation may be created.

Herein, we report the preparation of alternating copolymers containing fluorene and the ortho-pyridyl or ortho-pyrimidyl groups at the C-5 position of the oxadiazole ring. The oxadiazole derivative is placed at the *meta* position along the polymer main chain, therefore the resonance interaction from the oxadiazole center is only transmitted up to the *meta*-phenylene bridge. The molecular design, therefore, limits the resonance interaction between the oxadiazole and polymer backbone. This electronic connection could be exploited to attenuate the signal transfer between the oxadiazole sensing site and fluorescent polymer backbone [14]. This chelating ability and chelating mode should allow individual metal ions or a combination of them as input with fluorescence output in terms of both intensity and wavelength [15]. This was expected to couple with the 1,3,4-oxadiazole ring to form (O,N) or (N,N) bidentate chelation for metal ions.

2. Experimental

2.1. Instrumentation

¹H and ¹³C NMR spectra were recorded in deuterated chloroform on a Bruker AVIII 500 MHz spectrometer. (Abbreviations used: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad.) Electron Impact (EI) mass spectra were determined on Shimadzu LCMS-IT-TOF Mass Spectrometer. Elemental analysis was performed on a Heraeus varioIII-NCSH elemental analyzer. Gel permeation chromatography (GPC) was carried in THF solution using low polydispersity polystyrene standards for calibration with Water 2414 RI detector. UV-vis measurements were obtained on a Jasco V-670 UV-Vis-NIR spectrophotometer. Photoluminescence measurements were carried out on a Jasco FP6300 fluorescence spectrophotometer. Polymer thin films were spin-coated on a glass plate from tetrahydrofuran (THF) solution at 1000 rpm for 60 s. Thermal properties were studied by thermogravimetric analysis on a TA TGA Q500 at a heating rate of 10°C/min and differential scanning calorimetry on a Perkin-Elmer DSC4000 thermal analyzer at a heating or cooling rate of 10 °C/min. The melting point was recorded using MEL-TEMP 1001D melting point apparatus.

2.2. Materials

Unless otherwise noted, all reagents were used as received from Alfa or Aldrich without further purification. THF was distilled under a nitrogen atmosphere over sodium/benzophenone. The monomer **1**, 2,2'-(9,9-dioctyl-9*H*-fluorene-2,7-diyl)bis(4,4,5,5tetramethyl-1,3,2-dioxaborolane) was prepared by lithiation of the 2nd and 7th position of the dibromodioctyl substituted fluorene followed by addition with 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane. The reaction mixture was then warmed to room temperature and stirred for 18 h. The crude compound was purified by recrystallization in methanol and column chromatography. The 2-(5-(3,5-dibromophenyl)-1,3,4-oxzdiazol-2-yl)pyridine, **2**, and 2-(5-(3,5-dibromophenyl)-1,3,4-oxzdiazol-2-yl)pyrimidine, **3**, can be synthesized by a modification of established procedures [16].

2.2.1. Synthesis of 2,2'-(9,9-dioctyl-9H-fluorene-2,7diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1)

To a solution of 2,7-dibromo-9,9-dioctylfluorene (4.0 g, 7.3 mmol) in dry THF (80 mL) was added n-butyllithium (12 mL, 19.2 mmol, 1.6 M) dropwise over 10 min and the mixture was stirred at -78°C for 2h. 2-Isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (4.6 mL, 19.8 mmol) was then added and the resulting mixture was stirred for a further 1.5 h at -78 °C, allowed to warm to room temperature and stirred for a further 18 h. The reaction mixture was poured into water (200 mL), extracted with diethyl ether (100 mL), washed with water (2×50 mL) and dried with anhydrous MgSO₄. The solvent was evaporated and the crude product was purified by recrystallization from a solvent system of DCM and methanol and then by column chromatography using 5% of ethyl acetate and 95% of hexane as eluent to give white crystals in a yield of 67%. ¹H NMR (500 MHz, CDCl₃, δ): 7.81 (d, *J* = 7.5 Hz, 2H), 7.75 (s, 2H), 7.72 (d, J=7.5 Hz, 2H), 2.0 (m, 4H), 1.39 (s, 24H), 1.23–0.97 (m, 20H), 0.81 (t, J=7.2 Hz, 6H), 0.56 (m, 4H); ¹³C NMR (167 MHz, CDCl₃, δ): 150.30, 143.74, 133.21, 128.48, 118.92, 83.27, 54.73, 39.64, 31.33, 29.48, 28.74, 28.70, 24.49, 23.15, 22.14, 13.61. Mass spectrum (EI+, *m/z*) 643 (M⁺). m.p. 128 °C.

2.2.2. Synthesis of

2-(5-(3,5-dibromophenyl)-1,3,4-oxadiazol-2-yl)pyridine (2)

To a mixture of picolic acid (0.62 g, 5 mmol). 3,5-dibromobenzohydrazide (1.47 g, 5 mmol) and diisopropylethylamine (1.94 g, 15 mmol) in acetonitrile (80 mL) at room temperature was added O-(benzotriazol-1-yl)-N,N,N',N'tetramethyluronium tetrafluoroborate (1.77 g, 5.5 mmol) and the resulting mixture was stirred for 14 h. N,N-Diisopropylethylamine (1.3 g, 10 mmol) was successively added, followed by 4-methyl benzenesulfonyl chloride (2.86 g, 15 mmol) and the reaction mixture was stirred for 12 h before pouring into a 14% NH₃ aqueous solution. The crude mixture was stirred at room temperature for 30 min and then extracted with DCM and water. The organic layers were combined, washed with 2 M NaOH aqueous solution, dried over MgSO₄, filtered and evaporated. The residue was chromatographed using DCM as eluent to give a white solid in a yield of 58%. ¹H NMR (500 MHz, CDCl₃, δ): 8.84 (dd, *J* = 4.8, 1.0 Hz, 1H), 8.34 (d, J=7.8 Hz, 1H), 8.32(d, J=1.7 Hz, 2H), 7.94 (td, J=7.8, 1.0 Hz, 1H), 7.86 (t, J = 1.7 Hz, 1H), 7.52 (dd, J = 7.8, 4.8 Hz, 1H); ¹³C NMR (167 MHz, CDCl₃, δ): 164.33, 163.11, 150.39, 143.18, 137.34, 137.32, 128.69, 126.63, 126.14, 123.70, 123.50. Mass spectrum (EI+, *m/z*) 381 (M⁺). m.p. 206 °C.

2.2.3. Synthesis of

2-(5-(3,5-dibromophenyl)-1,3,4-oxadiazol-2-yl)pyrimidine (**3**)

To a mixture of pyrimidine-2-carboxylic acid (0.62 g, 5 mmol), 3,5-dibromo-benzohydrazide (1.47 g, 5 mmol) and diisopropylethylamine (1.94 g, 15 mmol) in acetonitrile (80 mL) at room temperature was added *O*-(benzotriazol-1-yl)-*N*,*N*,*N'*,*N'*tetramethyluronium tetrafluoroborate (1.77 g, 5.5 mmol) and the resulting mixture was stirred for 5 h. *N*,*N*-Diisopropylethylamine (1.3 g, 10 mmol) was successively added, followed by 4-methyl benzenesulfonyl chloride (2.86 g, 15 mmol) and the reaction mixture was stirred for 5 h before pouring into a 14% NH₃ aqueous solution. The crude mixture was stirred at room temperature for 30 min and then extracted with DCM and water. The organic Download English Version:

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