Polymer 54 (2013) 3542-3547

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Synthesis of water-soluble, fluorescent, conjugated polybenzodiazaborole for detection of cyanide anion in water

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ARTICLE INFO

Article history: Received 6 February 2013 Received in revised form 27 April 2013 Accepted 1 May 2013 Available online 9 May 2013

Keywords: Conjugated polymers Sensors Fluorescence

ABSTRACT

A polymer sensor (**P1**) containing benzodiazaborole moieties for recognition of cyanide anion and sulfonate groups for water-solubility was synthesized by Suzuki cross-coupling polymerization, which enables cyanide detection in aqueous solution. The polymer showed visible fluorescence quenching upon exposure to cyanide anion concentrations as low as $\sim 2 \,\mu$ M. Selective detection of cyanide anions can be accomplished via fluorescence quenching, while other anions exhibited fluorescence enhancement upon exposure, mainly due to the difference in the nucleophilicity of anions, affecting benzodiazaborole group. © 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Recognition and sensing systems for anions have received a great deal of interest because of their widespread use in biological, chemical, and environmental processes [1]. Among various anions, the cyanide anion is one of the most detrimental due to its toxicity toward biological and environmental systems [2]. The cyanide anion is extremely dangerous and can be absorbed through the lungs, skin, and gastrointestinal tract, leading to vomiting, loss of consciousness, and eventual death [3]. Because of the extreme toxicity of cyanide, the maximum contaminant level for free cyanide in drinking water should not exceed 2.7×10^{-6} M according to the World Health Organization (WHO) [4].

As a result, a variety of methods for cyanide detection have been reported using colorimetric and fluorometric detection methods. Various approaches related to the cyanide-complexes with transition metals [5a–d], CdSe quantum dots [5e,f], boronic acid derivatives [5g,h], and gold nanoclusters [5i,j]. Nucleophilic attack of cyanide to electron-deficient benzothiadiazole [6a], pyrylium salt [6b], oxazine [6c], acyl triazene [6d], acridinium [6e], and salicylaldehyde [6f,g] have been developed for cyanide detection. Along with the aforementioned methods of cyanide detection, electron-deficient boron-containing compounds have proven to be highly efficient in colorimetric and fluorescent cyanide detection [7a–d]. Anion recognition in the colorimetric and fluorescence response can be also dictated by the basicity of the anions, working on amino (N–H) groups such as urea moieties [7e–g].

It is known that conjugated polymers have remarkable efficiencies of signal amplification compared with the weak signals of their corresponding monomers, due to π - π * transitions of π -conjugated properties [8]. In general, conjugated polymers are hydrophobic in nature due to their rigid main chain, and thus, water-soluble conjugated polymers can be obtained by the incorporation of polar functional groups such as carboxyl groups, sulfonates, phosphonates, and quaternary ammonium salts onto the polymer backbone [9]. Water-soluble conjugated polymers, i.e. conjugated polyelectrolytes are being intensively studied for applications in biosensors or chemical sensors in an aqueous environment, because of their detection capabilities for DNA, proteins, and other biologically and chemically relevant molecules [10].

As mentioned above, most of the developments of cyanide sensors are focused on small molecules, while polymeric sensory materials are rarely reported. Furthermore, the majority of polymer sensory materials for cyanide anion are not soluble in water due to their organic and hydrophobic nature, preventing their application to aqueous samples [11].





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^{0032-3861/\$ -} see front matter © 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.polymer.2013.05.002

Herein, we report a rational design of a water-soluble conjugated polymer for the detection of cyanide anions via turn-off mode based on the interaction with benzodiazaborole group, which is composed of electron-deficient boron and acidic N-H units, which will be deprotonated by cyanide attack. Sulfonate groups were introduced in the side chains of the conjugated polymer to enhance water-solubility, thus making this design applicable to aqueous samples. The detection mechanism involves the fluorescence quenching of P1 in the presence of cyanide anions, presumably due to the combined interactions both between electron deficient boron and nucleophilic cyanide anions [5h,7a-d,11a,b,12] and between acidic amines and basic cyanide anions [7f,g]. To our knowledge, this is the first report to exploit both effects in cyanide anion sensing. As a result, the newly designed polymer could interact with cyanide anions with a high degree of selectivity (even in the presence of other anions) and sensitivity ($\sim 2 \mu M$) based on the change in their fluorescence intensity.

2. Experimental

2.1. Materials

All the chemicals were purchased from Aldrich and Acros and were used without further purification. 2,5-Dibromobenzene-1,4-diol (1) [13], 1,4-dibromo-2,5bis(4-sulfonatobutoxy) benzene sodium salt (2) [14], 4,7-dibromo-2,1,3-benzothiadiazole (3) [15], 3,6-dibromobenzene-1,2-diamine (4) [16], and 4,7-dibromo-2,3dihydro-2-phenyl-1H-benzo[d] [1,3,2]diazaborole (5) [12] were synthesized according to previously published methods.

2.2. Characterization

The ¹H, ¹³C, and ⁵B NMR spectra were obtained using a Bruker DRX-300 spectrometer with tetramethylsilane as an internal standard (Korea Basic Science Institute). The FT-IR spectra were obtained from a Bruker Tensor 27 spectrometer. The UV-vis absorption spectra were recorded on a PerkinElmer Lambda 35 spectrometer. Elemental analysis was performed on an Elemental Analyzer EA 1108 (Fisons Instruments). The photoluminescence spectra were obtained from a Cary Eclipse (Varian) fluorescence spectrophotometer utilizing a xenon lamp as the excitation source.

2.3. Synthesis

2.3.1. 2,5-Dibromohydroquinone (1)

Hydroquinone (10 g, 90.8 mmol) was dissolved in acetic acid (80 mL) in a 500 mL three-necked round-bottomed flask. A solution of Br₂ (9.34 g, 181.6 mmol) in acetic acid (30 mL) was added dropwise to the hydroquinone solution. The mixture was stirred at room temperature for 4 h after which water was added. The precipitate was isolated by filtration, and was crystallized from the aqueous solution. Yield 7.14 g (29%). ¹H NMR (300 MHz, DMSO-*d*₆): δ 9.82 (s, 2H), 7.04 (s, 2H) ppm. FT-IR (KBr, cm⁻¹): 1482 (C=C), 581 (C–Br).

2.3.2. 2,5-Dibromo-1,4-bis(4-sulfonatobutoxy)phenylene sodium salt (**2**)

Sodium hydroxide (0.895 g, 22.4 mmol) and **1** (2 g, 7.46 mmol) were dissolved in ethanol (17.5 mL) in a 250 mL three-necked round-bottomed flask. After the addition of 1,4-butane sultone (2.3 mL, 22.4 mmol), the reaction mixture was stirred and refluxed for 20 h. After the reaction, the crude product was isolated by filtration and was washed with ethanol. The product was dried *in*

vacuo. Yield 3.95 g (90.8%). ¹H NMR (300 MHz, DMSO-*d*₆): δ 7.43 (s, 2H), 4.00 (t, 4H), 3.08–3.03 (t, 4H), 1.78–1.69 (m, 8H) ppm. FT-IR (KBr, cm⁻¹): 3063 (C–H), 1479 (C=C), 1399 (SO₃), 586 (C–Br).

2.3.3. 4,7-Dibromo-2,1,3-benzothiadiazole (3)

2,1,3-Benzothiadiazole (1 g, 73.7 mmol) was dissolved in 47% hydrobromic acid (10 mL) in a 50 mL three-necked roundbottomed flask. A solution of bromine (1.14 mL, 22.02 mmol) in 47% hydrobromic acid (10 mL) was added dropwise into the solution. The mixture was refluxed and stirred for 4 h. Precipitates were isolated by filtration washed with water. The product was dried *in vacuo*. Yield 1.57 g (72.56%). ¹H NMR (300 MHz, CDCl₃): δ 7.73 (s, 2H) ppm. FT-IR (KBr, cm⁻¹): 3077–3046 (C–H), 1870 (C=N), 1479 (C=C), 586 (C–Br). Anal. Calcd for (C₆H₂Br₂N₂S): C, 24.5; H, 0.69; N, 9.53; S, 10.9. Found: C, 24.3; H, 0.70; N, 9.21; S, 11.0.

2.3.4. 3,6-Dibromobenzene-1,2-diamine (4)

3 (1 g, 3.40 mmol) was dispersed in ethanol (33 mL) in a 100 mL round-bottomed flask. Sodium borohydride (2.4 g, 63.4 mmol) was added portionwise at 0 °C. The mixture was stirred at room temperature for 20 h. After evaporating the solvent under vacuum, the solid product was dissolved in ether. The ether solution was washed with water several times, dried on sodium sulfate, and was finally removed by evaporation. The product was dried *in vacuo*. Yield 0.3 g (33%). ¹H NMR (300 MHz, CDCl₃): δ 7.27 (2H), 4.0 (4H) ppm. FT-IR (KBr, cm⁻¹): 3385 (NH₂), 3079 (C–H), 1648 (N–H), 1452 (C=C), 1240 (C–N). Anal. Calcd for (C₆H₆Br₂N₂): C, 27.1; H, 2.27; N, 10.53. Found: C, 27.5; H, 2.32; N, 10.4.

2.3.5. 4,7-Dibromo-2,3-dihydro-2-phenyl-1H-benzo[d] [1,3,2] diazaborole (**5**)

4 (0.3 g, 1.13 mmol) and phenylboronic acid (0.17 g, 1.356 mmol) were dissolved in toluene (8 mL) in a 50 mL three-necked roundbottomed flask. The mixture was refluxed and stirred for 3 days. After removing the solvent by evaporation under vacuum, a solid product was crystallization from hexane. The product was dried *in vacuo*. Yield 0.2 g (50%). ¹H NMR (300 MHz, DMSO-*d*₆): δ 8.02 (2H, s), 7.95 (2H, s), 7.77 (2H, d), 7.38 (1H, m), 7.32 (2H, t) ppm. ⁵B NMR (DMSO-*d*₆): δ –3.50 ppm. FT-IR (KBr, cm⁻¹): 3405 (N–H), 1870 (C=N), 1479 (C=C), 1420 (B–N), 586 (C–Br).

2.4. Polymerization of P1

2 (0.2109 g, 0.361 mmol), 5 (0.0317 g, 0.09 mmol), and 1,4benzenediboronic acid bis(pinacol) ester (0.1489 g, 0.451 mmol) were dissolved in a mixture of DMF (6 mL) and 2 M K₂CO₃ aqueous solution (9 mL) in a three-necked round-bottom flask. After addition of tetrakis(triphenylphosphine)palladium(0) (0.0266 g, 0.023 mmol) as a catalyst, the reaction mixture was stirred at 90 °C for 48 h under argon. After the reaction, the reaction mixture was cooled, poured into acetone (500 mL), and the precipitates were then isolated by filtration. Finally, the polymer was purified through dialysis against water (Millipore Nanopure™) using a 12.4 kD MWCO cellulose membrane for 3 days. After the dialysis, the polymer solution was freeze-dried and a dark yellow solid was obtained. ¹H NMR (300 MHz, DMSO- d_6): δ 8.0 (s, amine group), 7.8-6.9 (m, phenyl group), 4.1-3.6 (m, alkyl group), 3.1-2.5 (m, alkyl group), 2.0–1.6 (m, alkyl group) ppm. ¹³C NMR (75 MHz, DMSO-d₆): δ 159.67, 151.69, 141.25, 136.10, 135.69, 130.87, 127.46, 123.63, 120.14, 107.78, 55.35, 55.26, 25.38, 24.33, 24.10, 22.94, 22.88 ppm. ⁵B NMR (DMSO- d_6): δ –3.54 ppm. FT-IR (KBr, cm⁻¹): 3405 (N-H), 3063 (C-H), 1870 (C=N), 1479 (C=C), 1420 (B-N), 1399 (SO₃), Anal. Calcd. (%) for C_{19.6}H_{21.5}N_{0.33}S_{1.67}O_{5.0}K_{1.67}: C, 51.01; H, 4.69; N, 0.99; S, 11.56; Found: C, 50.00; H, 4.58; N, 1.0; S,10.98.

3. Results and discussion

3.1. Synthesis and photophysical properties

The synthetic procedures for the preparation for monomers and the polymer **P1** are illustrated in Scheme 1. 1.4-Dibromo-2.5bis(4-sulfonatobutoxy)benzene sodium salt (2) was synthesized according to the previously published methods [13], 4.7-Dibromo-2,1,3-benzothiadiazole (3) was easily obtained via bromination of commercially available 2,1,3-benzothiadiazole with a good yield [15]. 4,7-Dibromo-2,3-dihydro-2-phenyl-1H-benzo[d] [1,3,2]diazaborole (5) was obtained via the addition of phenylboronic acid into 4, in toluene [12]. P1 was synthesized with corresponding monomers via the palladium-catalyzed Suzuki cross-coupling reaction. Monomer **5** was used in this experiment to obtain 100% diazaborole units in the polymer, instead of the more common and simple usage of post-functionalization. According to the previous published method of post-functionalization with phenylboronic acid to a polymer, it was reported that only 73-85% of the transformation of diamino units to diazaborole units could be attained [12].

The molar composition in **P1** was determined by elemental analysis, and was found to be 0.18:0.82 as a mole fraction (m and n). The chemical structure of the polymer was confirmed by ¹H, ¹³C, and ⁵B NMR spectra.

Due to the large amounts of sulfonate groups, **P1** shows good solubility in water. However, it was not possible to obtain a reliable molecular weight of **P1**. Determination of molecular weight of **P1** by gel permeation chromatography (GPC) using an aqueous mobile phase was not possible, because of the adsorption of the polymer to the polystyrene gel in the GPC column. Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) was also



Fig. 1. Absorption (dotted) and fluorescence (solid) spectra of **P1** in aqueous solution (|**P1**| = 1 × 10⁻⁶ M for absorption spectrum). Excitation wavelength 323 nm.

attempted, but it was not possible to obtain a feasible data [10h,i,17]. However, it should be noted that the molecular weight of **P1** should be more than 12,400 because **P1** was dialyzed using a membrane of 12,400 cutoff.

The optical absorption and fluorescence emission spectra of the polymers in aqueous solution are shown in Fig. 1. **P1** has an absorption maximum at 323 nm in aqueous solution. The polymer exhibits blue emission in aqueous solution under UV irradiation and shows an emission maximum around 428 nm. The quantum yield of **P1** was found to be 3.4% in aqueous solution, which was determined by comparing with rhodamine B as a standard.



Scheme 1. Synthetic routes for monomers and polymer.



Fig. 2. Changes in absorbance (a) and emission (b) spectra of **P1** (1.5×10^{-5} M) with cyanide concentration of 0 (\bigcirc); 1.0×10^{-5} (\bigtriangledown); 1.0×10^{-4} (\blacklozenge); 1.0×10^{-3} M (\lhd) in aqueous solution; (c) changes in the fluorescence intensity of **P1** at 428 nm according to the concentration of cyanide anion.

3.2. Cyanide sensing properties

The interaction of **P1** and cyanide anions was investigated in aqueous media under ambient condition. The concentrations of **P1** was 1.5×10^{-6} M. Standard solutions of tetrabutylammonium cyanide with various concentrations of 1.0×10^{-7} to 1.0×10^{-3} M were added to the **P1** solution. Changes in the optical properties of **P1** were examined in 10 mm quartz cuvette.

The effect of the cyanide anion on the UV-vis absorption spectra is shown in Fig. 2a. As can be seen from the spectra, there were negligible changes in the absorbance and in the absorption maximum upon the addition of cyanide anions to the **P1** solution. In contrast, progressive emission quenching of **P1** at 428 nm was observed in the fluorescence spectra after the addition of cyanide anions as shown in Fig. 2b and c. A linear relationship between the intensity changes and logarithmic concentrations of cyanide anion



Fig. 3. Partial ¹H (left) and ⁵B NMR (right) spectra of 5 (a) and (b); $5 + CN^{-}$ (2 equiv) (c) and (d) in DMSO- d_6 .

can be observed with the naked-eye (inset photographs in Fig. 2c) under UV irradiation. The limit of detection (LOD) was determined to be about 2 μ M, as estimated according to a previously reported method [18].

¹H and ⁵B NMR titrations of monomer **5** were carried out upon addition of 2 equiv of cyanide anion to elucidate the deprotonation of N–H and electronic perturbation in boron atoms as shown in Fig. 3. It was possible to observe both disappearance of N–H peak at 8.02 ppm and chemical shift of boron peak (-3.50 to -3.95 ppm) in the presence of cyanide anion in DMSO-*d*₆ solution of **5**. Based on these observations, it is presumed that the fluorescence quenching was caused by the combined effects of electronic perturbation of boron atoms as well as deprotonation of N–H in the presence of cyanide anion.



Fig. 4. (a) Changes in the emission spectra, (b) relative emission changes, and (c) photographs of **P1** (1.5 × 10⁻⁵ M) in aqueous solution by addition of anions (1.0 × 10⁻⁵ M). Excitation wavelength 323 nm. ($\Delta I = I_0 - I$, $I_0 =$ initial intensity of **P1** solution at 428 nm, I = intensity of **P1** + anion at 428 nm).

The crucial feature of **P1** lies in its high selectivity toward cyanide anion over the other competitive anions. Changes in the fluorescence spectra of **P1** $(1.5 \times 10^{-5} \text{ M})$ are completely different between cyanide and other anions such as F⁻, Br⁻, Cl⁻, I⁻, AcO⁻, and PO₄⁻ in aqueous solution. As can be seen in Fig. 4, the competitive anions show noticeable enhancement in fluorescence intensity at 428 nm, while only cyanide anion lead to quenching the fluorescence of **P1**. This phenomenon can be clearly seen by measuring the relative intensity changes in Fig. 4b in the presence of cyanide and of other anions. It is likely that the alteration in hydrogen bonding between the electron-rich amine and anions is responsible for the increase in the emission intensities when **P1** was exposed to F⁻, Br⁻, Cl⁻, I⁻, AcO⁻, and PO₄⁻ [19].

The high selectivity of **P1** is much highlighted by competition experiments in mixed anions (cyanide + anion). In the presence of other competitive anions, cyanide can still quench the fluorescence of **P1**, meaning there is no interference by other anions (Fig. 5a). This negligible interference from other anions suggests that the **P1** has significant selectivity toward cyanide anion. Judging from less



Fig. 5. (a) Changes in the fluorescence and (b) relative intensity of **P1** in aqueous solution $(1.5 \times 10^{-5} \text{ M})$ with mixed anions $([\text{anion}] = 1.0 \times 10^{-5} \text{ M}; [\text{CN}^-] = 1.0 \times 10^{-5} \text{ M})$. Excitation wavelength 323 nm ($\Delta I = I_0 - I$, $I_0 =$ initial intensity of **P1** at 428 nm and I = intensity of **P1** + anions at 428 nm).

than 10% interference by other anions on the emission intensity, this enables **P1** to use as a highly selective material toward cyanide anion (Fig. 5b).

4. Conclusions

A new water-soluble conjugated polybenzodiazaborole based on boron moieties with sulfonate side chains was synthesized by Suzuki coupling polymerization for the creation of turn-off fluorescence sensor for cyanide anions. The conjugated polymer can interact with cyanide anions leading to fluorescence quenching, which was attributed to the interaction with electron-deficient boron atoms and cyanide anions. In contrast, anions other than cyanide had obvious response signals of fluorescence enhancement. This reveals that **P1** has good selectivity towards the cyanide anions based on the efficient fluorescence quenching. This specific approach enables us to attain a versatile tool for detecting cyanide anions. The newly synthesized water-soluble polymer is suitable for the sensitive and selective determination of cyanide anions.

Acknowledgments

This research was supported by Basic Science Research Program (2012R1A2A2A01004979) and Nuclear R&D Project through the National Research Foundation of Korea (NRF) funded by the Korean government.

References

- (a) Gunnlaugsson T, Glynn M, Tocci GM, Kruger DE, Pfeffer FM. Coord Chem Rev 2006;250:3094–117;
 - (b) Yoon J, Kim SK, Singh NJ, Kim KS. Chem Soc Rev 2006;35:355-60;
 - (c) Martínez-Máñez R, Sancanón F. Chem Rev 2003;103:4419-76;
 - (d) Gale PA. Acc Chem Res 2006;39:465-75;
 - (e) Beer PD, Gale PA. Angew Chem Int Ed 2001;40:486-516;
 - (f) Kim SK, Lee DH, Hong J-I, Yoon J. Acc Chem Res 2009;42:23-31;
 - (g) de Silva AP, Gunaratne HQN, Gunnlaugsson TA, Huxley TM, McCoy CP, Rademacher JT, et al. Chem Rev 1997;97:1515–66.
- [2] Kulig KW. Cyanide toxicity. Atlanta, GA: U. S. Department of Health and Human Services; 1991.
- (a) Baskin SI, Brewer TGSidell F, Takafuji ET, Franz DR, editors. Medical aspects of chemical and biological warfare. Washington DC: TMM Publication; 1997. p. 271–86. [Chapter 10];
 - (b) Baird C, Cann M. Environmental chemistry. New York: Freeman; 2005.
- [4] Guidelines for drinking-water quality. 3rd ed. Geneva: World Health Organization; 2004.
- [5] (a) Kim Y-H, Hong J-I. Chem Commun 2002:512-3;
 - (b) Chow CF, Lam MHW, Wong M-Y. Inorg Chem 2004;43:8387–93;
 (c) Anzenbacher Jr P, Tyson DS, Jursiková K, Castellano FN. J Am Chem Soc 2002:124:6232–3:
 - (d) Chung S-Y, Nam S-W, Lim J, Park S, Yoon J. Chem Commun 2009:2866–8; (e) Touceda-Varela A, Stevenson EI, Galve-Gasión JA, Dryden DTF, Mareque-Rivas JC. Chem Commun 2008:1998–2000;
 - (f) Jin WJ, Fernández-Argüelles JM, Costa-Femández JM, Pereiro R, Sanz-Medel A. Chem Commun 2005:883–5;
 - (g) Badugu R, Lakowicz JR, Geddes CD. J Am Chem Soc 2005;127:3635-41;
 - (h) Badugu R, Lakowicz JR, Geddes CD. Dyes Pigm 2005;64:49-55;
 - (i) Liu Y, Ai K, Cheng X, Huo L, Lu L. Adv Funct Mater 2010;20:951-6;
 - (j) Zhai Y, Jin L, Wang P, Dong S. Chem Commun 2011;47:8268-70.

- [6] (a) Qian G, Li X, Wang ZY. J Mater Chem 2009;19:522–30;
 (b) García-Acosta B, Martínez-Máñez R, Sancenón F, Soto J. Chem Commun
 - 2005:2790–2; (c) Tomasulo M, Sortino S, White AJP, Raymo FM. J Org Chem 2006;71: 744–53:
 - (d) Chung Y, Lee H, Ahn KH. Org Lett 2003;5:4003-6;
 - (e) Yang Y-K, Tae J. Org Lett 2006;8:5721–3;
 - (f) Lee K-S, Kim H-J, Kim G-H, Shin I, Hong J-I. Org Lett 2008;10:49–51; (g) Kwon SK, Kou S, Kim HN, Chen X, Hwang H, Nam S-W, et al. Tetra-
- hedron Lett 2008;49:4102–5. [7] (a) Gulivev R. Ozturk S. Sahin E. Akkava EU. Org Lett 2012:14:1528–31:
- (b) Palomares E, Martínez-Díaz MV, Torres T, Coronado E. Adv Funct Mater 2006;16:1166-70;
 - (c) Ros-Lis JV, Martínez-Máñez R, Soto J. Chem Commun 2005:5260-2;
 - (d) Ekmekci Z, Yilmaz MD, Akkaya EU. Org Lett 2008;10:461-4;
 - (e) Sakai R, Sakai N, Satoh T, Li W, Zhang A, Kakuchi T. Macromolecules 2011;44:4249–57;
 - (f) Vallejos S, Estévez P, García FC, Serna F, de la Peña JL, García JM. Chem Commun 2010;46:7951–3;
 - (g) Jiang J, Xiao X, Zhao P, Tian H. J Polym Sci Part A: Polym Chem 2010;48: 1551–6.
- [8] (a) Skotheim TA, Elsenbaumer RL, Reynolds JDekker M, editor. Handbook of conducting polymers. 2nd ed. 1997. New York;
 (b) Haddiagram G, una Handbook DEM Wave GG, him a contract in the second secon
 - (b) Hadziioannou G, van Hutten PFMalliaras GG, editor. Semiconducting polymers. Weinheim, Germany: Wiley: 2000;
 - (c) Chandrasekhar P. In: Conducting polymers, fundamentals and applications. Boston: Kluwer; 1999.
- [9] (a) Swager TM. Acc Chem Res 1998;31:201-7;
 - (b) Thomas III SW, Joly GD, Swager TM. Chem Rev 2007;107:1339-86;
 - (c) Bunz UHF. Chem Rev 2000;100:1605-44;
 - (d) Liu B, Bazan GC. Chem Mater 2004;16:4467-76;
 - (e) Ho H-A, Najari A, Leclerc M. Acc Chem Res 2008;41:168-78.
- [10] (a) Gaylord BS, Heeger AJ, Bazan GC. Proc Natl Acad Sci U S A 2002;99: 10954-7;
 - (b) Wang S, Gaylord BS, Bazan GC. J Am Chem Soc 2004;126:5446-51;
 - (c) Liu B, Bazan GC. J Am Chem Soc 2006;128:1188-96;
 - (d) Lee K, Povlich LK, Kim J. Adv Funct Mater 2007;17:2580-7;
 - (e) Kwak CK, Kim DG, Kim TH, Lee C-S, Lee M, Lee TS. Adv Funct Mater 2010;20:3847–55;
 - (f) Kim J, McQuade DT, McHugh SK, Swager TM. Angew Chem Int Ed 2000;39:3868-72;
 - (g) Lee JH, Kim DG, Kwon NY, Jang GS, Son JH, Lee M, et al. J Polym Sci Part A: Polym Chem 2011;49:138–46;
 - (h) Kwon NY, Kim D, Son JH, Jang GS, Lee JH, Lee TS. Macromol Rapid Commun 2011;32:1061–5;
 - (i) Kwon NY, Kim D, Jang G, Lee JH, So J-H, Kim C-H, et al. ACS Appl Mater
 - Interfaces 2012;4:1429–33.
- [11] (a) Li H, Jäkle F. Macromol Rapid Commun 2010;31:915–20;
 (b) Sakai R, Nagai A, Tago Y, Sato S, Nishimura Y, Arai T, et al. Macromolecules 2012;45:4122–7;

(c) Li Z, Lou X, Yu H, Li Z, Qin J. Macromolecules 2008;41:7433-9;

- (d) Lou X, Qiang L, Qin J, Li Z. ACS Appl Mater Interfaces 2009;1:2529-35;
- (e) Wu X, Xu B, Tong H, Wang L. Macromolecules 2011;44:4241-8.
- [12] Yamaguchi I, Choi B-J, Koizumi T, Kubota K, Yamamoto T. Macromolecules 2007;40:438–43.
- [13] Yang R, Tian R, Yan J, Zhang Y, Yang J, Hou Q, et al. Macromolecules 2005;38: 244–53.
- [14] Hou Q, Xu Y, Yang W, Yuan M, Peng J, Cao Y. J Mater Chem 2002;12: 2887–92.
- [15] Vetrichelvan M, Hairong L, Ravindranath R, Valiyaveettil S. J Polym Sci Part A: Polym Chem 2006;44:3763–77.
- [16] Kim HJ, Lee JH, Lee M, Lee TS. React Funct Polym 2008;68:1696-703.
- [17] (a) Bao Y, Li Q, Liu B, Du F, Tian J, Wang H, et al. Chem Commun 2012;48: 118–20;
 - (b) Kim S, Jackiw J, Robinson E, Schanze KS, Reynolds JR, Baur J, et al. Macromolecules 1998;31:964–74.
- [18] (a) Thomsen V, Schatzlein D, Mercuro D. Spectroscopy 2003;18:112–4;
- (b) http://goldbook.iupac.org/L03540.html.
- [19] Nishiyabu R, Anzenbacher Jr P. Org Lett 2006;8:359-62.