Title	Electrofluorochromic detection of cyanide anions using a benzothiadiazole-containing conjugated copolymer
Author(s)	Ding, Guoqiang; Zhou, Hui; Xu, Jianwei; Lu, Xuehong
Citation	Ding, G., Zhou, H., Xu, J., & Lu, X. (2013). Electrofluorochromic detection of cyanide anions using a benzothiadiazole-containing conjugated copolymer. Chemical communications, 50(6), 655-657.
Date	2014
URL	http://hdl.handle.net/10220/24461
Rights	© 2014 The Royal Society of Chemistry. This is the author created version of a work that has been peer reviewed and accepted for publication by Chemical Communications, The Royal Society of Chemistry. It incorporates referee's comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [http://dx.doi.org/10.1039/c3cc47732k].

ARTICLE TYPE

Electrofluorochromic Detection of Cyanide Anion with A Benzothiadiazole-Containing Conjugated Copolymer

**Guoqiang Ding,[a] Hui Zhou,[b] Jianwei Xu,*[b] and Xuehong Lu*[a]**

Selective detection of cyanide anion is realized via electrofluorochromism of a benzothiadiazole-containing conjugated copolymer because oxidative fluorescence quenching induced by positive potentials can be significantly
10 **weakened by interaction between nucleophilic cyanide and electron-deficient benzothiadiazole.**

Electrofluorochromism, known as the reversible change in fluorescence emission induced by external electric potentials, has attracted increased attention recently.[1-7] Electrofluorochromic
15 (EFC) materials are promising candidates for various applications such as sensing and fluorescence imaging. For example, Voicescu *et al.* reported the detection of a protein redox state based on the tryptophan fluorescence emission.[8] Common EFC materials include molecular dyads, conjugated polymers and intrinsically
20 switchable fluorophores.[9] Compared with the other two types of EFC materials, the conjugated polymers show the ability to amplify their sensitivity in fluorescence responses owing to the efficient electronic delocalization and rapid transport of excitons along the π-conjugated backbone.[10-13] Compared with
25 electrochromic polymers that are intensively studied, EFC conjugated polymers are, however, still a sparsely investigated field. The first report on electrochemically switchable intrinsic electroactive fluorophore appeared in 2004.[1] A few years later, Montilla *et al.* reported EFC properties of phenylene–vinylene
30 polymers.[3] More recently, dynamically controllable electrofluorochromism of electropolymerized poly(N-alkyl-2,7-di(2-thienyl)carbazole) was demonstrated by Goto *et al.*[6] Leung *et al.* reported that by blending two EFC conjugated polymers in a device, their fluorescence in yellow and blue regions could be
35 simultaneously quenched under a low potential.[7]

Cyanide anion (CN^-) exhibits high toxicity in physiological systems and is a dangerous environmental pollutant. Thus, various colorimetric and fluorometric detection methods for CN^- have been developed. Free CN^- form complexes with transition
40 metals,[14] CdSe quantum dots,[15] boronic acid derivatives,[16] or gold nanoclusters,[17] providing a common approach to chemosensors. Due to its strong nucleophilicity, nucleophilic attack of CN^- to electron-deficient compounds, such as benzothiadiazole,[18] pyrylium salt,[19] trifluoroacetophenone[20] and acridinium,[21] offers
45 an alternative approach. Some reported CN^- detection methods show high sensitivity and selectivity among many anions.[18, 21]

Enlightened by the aforementioned detection methods that utilize the strong nucleophilicity of CN^-, we synthesized a novel EFC conjugated copolymer that contains electron-deficient 2,1,3-
50 benzothiadiazole (BTD) for detection of CN^-. The use of an EFC conjugated copolymer for cyanide detection allows adjusting electronic structure of the chromophore, and hence may lead to more sensitive detection than that offered by traditional chemosensors. Herein we demonstrate EFC properties of this
55 copolymer and its capability for sensitive yet selective detection of CN^-. To the best of our knowledge, this is the first demonstration of EFC detection of CN^-, and EFC detection of other chemicals was also rarely reported.

Scheme 1 shows the structure of the copolymer (**P**) and its
60 synthesis route. The synthesis procedures are described in S3†. It can be seen that besides BTD, **P** also contains N-octyl-3,6-carbazole (C) and 3-hexylthiophene (HT) units. Carbazole is a common electron donor, which is often used as a fluorophore due to its ease in functionalization on N position for improving
65 solubility and good hole-transport ability.[22, 23] 3-Hexylthiophene is incorporated as chromophore separators and to further enhance solubility. Since both monomers are of A–B–A type, they can form an alternating copolymer, poly(C–BTD–C-*co*-HT–C–HT), via Suzuki coupling. The structures of the monomers were
70 verified by nuclear magnetic resonance (NMR) spectroscopy and mass spectroscopy (S3†). The structure of **P** was characterized by NMR spectroscopy and elemental analysis (S3†). In the ^{1}H NMR spectrum of **P** (Fig. S1†), the peak at 4.32 ppm corresponds to N-CH_2 in carbazole, while the peak at 2.79 ppm corresponds to CH_2
75 directly bonded to the thiophene ring (C-CH_2). The integration ratio of the two peaks is 3/2, which is consistent with that calculated from the repeating unit structure of **P**, confirming the successful synthesis of the copolymer. SEC measurement of **P** gives the apparent number-average molecular weight $M_n =$
80 13,400 Da (ca. 10 repeating units), with polydispersity index of 1.10. **P** shows good solubility in common solvents such as chloroform, toluene and *p*-xylene, which is attributed to the alkyl side chains in carbazole and thiophene units.
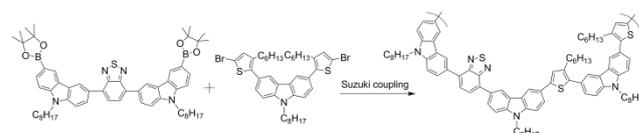
85 **Scheme 1** Synthesis route of the copolymer **P**.

Fig. 1a shows UV–vis absorption and photoluminescence (PL) spectra of **P** in solution and thin film form, respectively. The solution exhibits an absorption band at 315 nm, a shoulder at 350 nm and another band at 450 nm. The thin film shows a similar spectrum except that the band at 450 nm is red-shifted to 465 nm probably owing to inter-chain π–π stacking in the film. The band at 315 nm corresponds to carbazole units, while the band at 465 nm for thin film (450 nm for solution) can probably be attributed to π–π* transition of C-BTD-C moiety.[22, 24] The shoulder at 350 nm possibly arises from the interactions between HT and carbazole units. Despite the slight red-shift for the band corresponding to BTD, the PL peaks obtained by exciting at 450 nm for the solution and 465 nm for the film are both at 580 nm. In comparison with the solution, the thin film only shows slight fluorescence quenching because alkyl chains in carbazole and HT units hinder π–π stacking of adjacent chains.

Cyclic voltammograms (CV) of the spin-coated **P** thin film on indium tin oxide/poly(ethylene terephthalate) (**P**/ITO/PET) was conducted in a three-electrode electrochemical cell using platinum (Pt) wire as counter electrode, silver (Ag) wire as reference electrode, and 0.1 M LiClO$_4$/acetonitrile (ACN) as electrolyte. The details for the CV and spectroelectrochemical tests are given in S4†. The CV curves in Fig. 1b show that **P** exhibits an oxidation peak at 0.94 V and a shoulder peak at 1.10 V, and two reduction peaks at 0.52 and 0.80 V, respectively. Two pairs of redox peaks are typical for N-alkyl substituted 3,6-polycarbazole, which correspond to the radical cation and dication states, respectively.[25] It is interesting to note that the two oxidation (shoulder) peaks are fairly close to each other, indicating a relatively easy transition from the state of radical cation to dication. This phenomenon can be attributed to the electron-deficient BTD that facilitates electron removal from electron-rich carbazole and reduces its oxidation potential.[26]
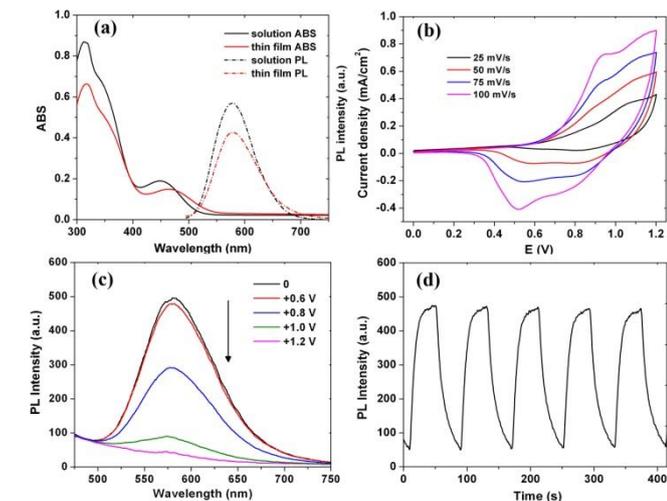
P exhibits both electrochromism and electrofluorochromism. The intensity of the absorption peak at 465 nm increases with

positive potential owing to oxidation (Fig. S2a†), and it can be repeatedly switched by applying an oscillating potential (Fig. S2b†). Upon increasing positive potential, the PL intensity (λ_{em} = 580 nm) of **P** is gradually reduced due to oxidative quenching, as shown in Fig. 1c. The PL intensity starts to reduce at 0.6 V, and falls to as low as around 20% of the maximum value when the oxidation potential reaches 1.0 V. This is consistent with the CV results that the oxidation becomes significant when the potential exceeds the first oxidation peak at 0.94 V. The fluorescence could recover when a negative potential is applied, and the switching is repeatable (Fig. 1d). The fluorescence quenching of **P** is due to electrochemical oxidation as when photo-excited, the oxidized chains would undergo non-radiative exciton decay, rather than energy relaxation via a radiative pathway.[6] By exciting at 465 nm, the C-BTD-C moiety is likely to be the main fluorophore that determines the fluorescence intensity at different states, whereas the carbazole unit between the two HT units is believed to play the role of fluorophore separator (together with the HT units).

Detection of CN$^-$ by fluorescent polymers is commonly conducted in solutions. In this work, we developed a different cyanide detection approach. Firstly, a **P**/ITO/PET electrode was inserted into a three-electrode electrochemical cell: a quartz cuvette filled with 0.1 M LiClO$_4$/ACN (reference electrolyte, **R**) with Pt wire as counter electrode and Ag wire as reference electrode, and a fluorescence spectrometer was used to record PL intensities (λ_{exc} = 465 nm, $\lambda_{monitor}$ = 580 nm) under a series of positive potentials provided by an electrochemical workstation. When the system reached equilibrium state at zero potential, the stabilized PL intensity was recorded as I$_0$. For a certain potential, the ratio of the PL intensity detected at equilibrium state, I, to I$_0$ is defined as normalized intensity. I/I$_0$ obtained at different potentials were plotted against potential, E, as shown by the black curve (■) in Fig. 2a. Then the **P**/ITO/PET electrode was inserted into another cell that contained **R** with a certain concentration of tetrabutylammonium cyanide (TBACN), and the stabilized PL intensities were recorded under the same series of potentials. The normalized intensities were calculated and plotted against E again. Three I/I$_0$–E curves corresponding to CN$^-$ concentrations of 10^{-6}, 10^{-5} and 10^{-4} M, respectively, are shown in Fig. 2a.

It can be seen that with **R** only, the normalized intensity decreases with increasing positive potential due to oxidative quenching. However, with **R** + TBACN, the normalized intensities are higher than that without TBACN at all positive

potentials (0.7-1.0 V), indicating that the oxidative quenching is significantly weakened in the presence of TBACN. In particular, it is striking to see that when the potential is above 0.9 V, even 1 μM of TBACN can induce a significant change in normalized PL intensity. This phenomenon probably results from the partial reduction of **P** owing to the interaction between nucleophilic CN⁻ and electron-deficient BTD. From Fig. 2a it is also observed that the higher the TBACN concentration, the higher the normalized intensity, i.e., the effect of oxidative quenching is weakened more at higher TBACN concentrations. Thus, the I/I_0–E curves corresponding to different cyanide concentrations may be used as calibration curves to determine cyanide concentrations of various analytes. Like in **R**, the PL intensity of **P** in **R** + TBACN could also be completely recovered under negative potentials (Fig. S3†). In addition, after cycling in **R** + TBACN (10^{-4} M), the **P**/ITO/PET electrode was washed in ACN, and put into **R** again. It could exhibit the original EFC switching curve corresponding to **R** (Fig. S4†), indicating that CN⁻ can be easily removed from the electrode and the interaction between CN⁻ and **P** is a physical interaction. Moreover, the electrolyte composed of 0.1 M LiClO$_4$ dissolved in ACN/H$_2$O (v/v = 1:1) was also used for CN⁻ detection (for TBACN concentrations up to 10^{-4} M) and similar phenomena were observed (Fig. S5†). Since H$_2$O and ACN are miscible, the above results imply that the cyanide concentration of an aqueous solution may be determined by mixing the aqueous solution with the reference electrolyte at a certain ratio and then using the mixed solution as the electrolyte in EFC detection tests.

To check whether CN⁻ could be selectively detected by this system, other anions including tetrabutylammonium (TBA)-based hydroxide (OH⁻), fluoride (F⁻), chloride (Cl⁻), bromide (Br⁻), iodide (I⁻), acetate (AcO⁻), nitrate (NO$_3$⁻) and bisulfate (HSO$_4$⁻) (10^{-5} M for each type of anion) were added together into **R**. As shown in Fig. 2b, the PL intensity changes upon oxidative quenching are almost the same for the electrolytes with and without these anions. This confirms that it is CN⁻, rather than TBA cation, that dominates the PL intensity of **P** upon oxidative quenching. Furthermore, by adding higher concentrations of OH⁻ and F⁻ (10^{-4} M for each) into **R**, still no significant change in I/I_0–E curves could be observed (Fig. S6†). This demonstrates that the detection is selective towards CN⁻ over other common nucleophilic anions. To further verify selectivity of the system, TBACN (10^{-4} M) was added into the electrolyte containing the eight types of other anions. It is observed that in this electrolyte, the normalized PL intensities of **P** under various potentials are similar to that in **R** + 10^{-4} M TBACN, further confirming the selectivity of the system towards CN⁻. The specific interaction of CN⁻ with **P** is probably a type of anion–π interactions. Such energetically favorable non-covalent interactions could exist between an electropositive aromatic ring and a nucleophilic anion.[27, 28] At oxidized state, BTD ring would be highly electron-deficient. Although OH⁻ and F⁻ are also fairly nucleophilic, based on our results only CN⁻ has significant interaction with oxidized **P**. This may be attributed to the stronger nucleophilicity of CN⁻ and the presence of triple bond in CN⁻. The triple bond may provide electron-rich π system for non-covalent interaction with electron-deficient π system of BTD, leading to charge transfer between CN⁻ and BTD (π^-–π^+ interaction) and hence weakening the oxidative quenching. More studies will be conducted in future to verify the mechanism proposed above.

In summary, we have synthesized a new EFC conjugated copolymer. Electrochemical oxidation of the copolymer induces severe fluorescence quenching when the potential is above 0.9 V. Moreover, the oxidative quenching is significantly weakened when TBACN is added into the electrolyte owing to the strong interactions between nucleophilic CN⁻ and electron-deficient BTD. The CN⁻ detection using this system is sensitive and selective, offering a promising route for CN⁻ sensing. The approach may also be extended to design other conjugated polymers for detection of other ions or molecules.

Notes and references

^{a} *School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore. Email: asxhlu@ntu.edu.sg.*

^{b} *Institute of Materials Research and Engineering, 3 Research Link, 117602, Singapore. Email: jw-xu@imre.a-star.edu.sg.*

1. M. Dias, P. Hudhomme, E. Levillain, L. Perrin, Y. Sahin, F.-X. Sauvage and C. Wartelle, *Electrochem. Commun.*, 2004, **6**, 325.
2. Y. Kim, E. Kim, G. Clavier and P. Audebert, *Chem. Commun.*, 2006, 3612.
3. F. Montilla and R. Mallavia, *J. Phys. Chem. B*, 2006, **110**, 25791.
4. F. Miomandre, R. Meallet-Renault, J.-J. Vachon, R. B. Pansu and P. Audebert, *Chem. Commun.*, 2008, 1913.
5. S. Seo, Y. Kim, Q. Zhou, G. Clavier, P. Audebert and E. Kim, *Adv. Funct. Mater.*, 2012, **22**, 3556.
6. K. Kawabata and H. Goto, *Chem. Eur. J*, 2012, **18**, 15065.
7. C.-P. Kuo, C.-N. Chuang, C.-L. Chang, M.-k. Leung, H.-Y. Lian and K. C.-W. Wu, *J. Mater. Chem. C*, 2013, **1**, 2121.
8. M. Voicescu, D. Rother, F. Bardischewsky, C. G. Friedrich and P. Hellwig, *Biochemistry*, 2010, **50**, 17.
9. P. Audebert and F. Miomandre, *Chem. Sci.*, 2013, **4**, 575.
10. Q. Zhou and T. M. Swager, *J. Am. Chem. Soc.*, 1995, **117**, 7017.
11. T. M. Swager, *Acc. Chem. Res.*, 1998, **31**, 201.
12. J.-S. Yang and T. M. Swager, *J. Am. Chem. Soc.*, 1998, **120**, 5321.
13. S. Wang, B. S. Gaylord and G. C. Bazan, *J. Am. Chem. Soc.*, 2004, **126**, 5446.
14. Y.-H. Kim and J.-I. Hong, *Chem. Commun.*, 2002, 512.
15. P. Anzenbacher, D. S. Tyson, K. Jursíková and F. N. Castellano, *J. Am. Chem. Soc.*, 2002, **124**, 6232.
16. W. J. Jin, M. T. Fernández-Argüelles, J. M. Costa-Fernández, R. Pereiro and A. Sanz-Medel, *Chem. Commun.*, 2005, 883.
17. Y. Liu, K. Ai, X. Cheng, L. Huo and L. Lu, *Adv. Funct. Mater.*, 2010, **20**, 951.
18. S. Dong, D. Ou, J. Qin and Z. Li, *J. Polym. Sci. A Polym. Chem.*, 2011, **49**, 3314.
19. F. García, J. M. García, B. García-Acosta, R. Martínez-Máñez, F. Sancenón and J. Soto, *Chem. Commun.*, 2005, 2790.
20. Y. M. Chung, B. Raman, D.-S. Kim and K. H. Ahn, *Chem. Commun.*, 2006, 186.
21. Y.-K. Yang and J. Tae, *Org. Lett.*, 2006, **8**, 5721.
22. J. Huang, Y. Niu, W. Yang, Y. Mo, M. Yuan and Y. Cao, *Macromolecules*, 2002, **35**, 6080.
23. N. Blouin and M. Leclerc, *Acc. Chem. Res.*, 2008, **41**, 1110.
24. K. M. Omer, S.-Y. Ku, J.-Z. Cheng, S.-H. Chou, K.-T. Wong and A. J. Bard, *J. Am. Chem. Soc.*, 2011, **133**, 5492.
25. D. Witker and J. R. Reynolds, *Macromolecules*, 2005, **38**, 7636.
26. G. Ding, C. M. Cho, C. Chen, D. Zhou, X. Wang, A. Y. X. Tan, J. Xu and X. Lu, *Org. Electron.*, 2013, **14**, 2748.
27. C. Garau, A. Frontera, D. Quiñonero, P. Ballester, A. Costa and P. M. Deyà, Anion-π Interactions, *Recent Research Developments in*

Chemical Physics, ed. S. G. Pandalai, Transworld Research Network, Kerala, India, 2004, vol. 5, pp. 227.

28. H. T. Chifotides and K. R. Dunbar, *Acc. Chem. Res.*, 2013, **46**, 894.

5