An imidazole-functionalized polyacetylene: convenient synthesis and selective chemosensor for metal ions and cyanide†

Qi Zeng,[a] Ping Cai,[a] Zhen Li,*[a] Jingui Qin[a] and Ben Zhong Tang[b]

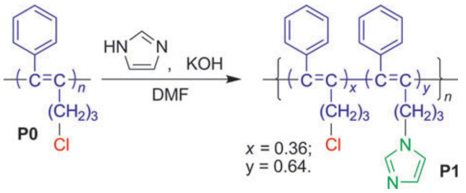
Received (in Cambridge, UK) 16th November 2007, Accepted 11th January 2008
First published as an Advance Article on the web 29th January 2008
DOI: 10.1039/b717764j

A new light-emitting polyacetylene bearing imidazole moieties in the side chain (P1), was conveniently prepared through a post-functionalization strategy, as a sensory polymer to selectively report the presence of Cu^{2+} (with a detection limit of 1.48 ppm) based on the fluorescence "turn-off". Interestingly, the quenched luminescence of P1 by Cu^{2+} could be turned on after the addition of CN^-, making P1 a novel, sensitive, and selective cyanide probe.

Polyacetylene (PA) is the archetypal conjugated polymer, and has attracted increasing interest in recent years. Thanks to the enthusiastic efforts of scientists, research has extended from the initial traditional conductive polyacetylene to liquid crystals, polymeric light-emitting diodes, helical polymers, gas separation membranes, organic–inorganic hybrids, nonlinear optical and magnetic materials *etc.*[1,2] Structurally, PA is a linear polyene chain [–(HC=CH)$_n$–]. The existence of two hydrogen atoms in its repeat unit offers ample opportunity to decorate the backbone with pendants: replacement of hydrogen in each repeat unit by one or two substituents yields monosubstituted (**1**) and disubstituted (**2**) PAs, respectively. We have been interested in functionalizing PA at the molecular level and have successfully polymerized hundreds of monosubstituted acetylenes containing a variety of functional groups. Disubstituted PAs are generally superior to their monosubstituted counterparts in performance: for example, poly(1-phenyl-1-octyne), a disubstituted PA, strongly resists thermal decomposition (no molecular weight change detectable after annealing in air at 120 °C for 20 h) and efficiently emits blue light, while poly(phenylacetylene), a monosubstituted PA, readily degrades and emits weakly.[3] The stability and strong luminescence of disubstituted PAs make them good candidates for polymer chemosensors, since the "molecular wire effect" in conjugated polymers usually greatly enhances the sensitivity of the polymer-based chemosensors due to the enhanced electronic communication among them.[4] However, there are very few reports concerning the properties of disubstituted PAs as chemosensors.[5] The reason might be partially the difficulties encountered in their synthesis. Generally, conjugated polymer-based chemosensors should contain some acceptor groups to trap the metal ions, such as bipyridyl, terpyridyl, and quinoline segments.[6] However, it is still a big challenge to prepare disubstituted PAs containing those moieties, as well as groups such as amide, amine, hydroxyl, cyano, thio, *etc.*

Very recently, partially based on our previous work[7] on polymer reactions, we have developed some synthetic routes to obtain some functional disubstituted PAs inaccessible by the direct polymerization of their monomers. Most of them contain highly polar side chains, such as azo moieties, indole groups and pyridine groups.[8] These results prompted us to design disubstituted PA chemosensors by using a postfunctionalization strategy. In this paper, we report the realization of this goal, and describe an imidazole-functionalized disubstituted polyacetylene **P1** (Scheme 1), which combines the advantages of the strong luminescence of disubstituted polyacetylenes and the metal ion-coordinating ability of imidazoles, to provide a novel kind of highly effective chemosensor. **P1** can report the presence of Cu^{2+} selectively based on the fluorescence "turn-off". Very interestingly, it can also indirectly probe the presence of trace CN^- both selectively and sensitively.

As shown in Scheme 1, **P1** was easily obtained from the reaction between **P0** and imidazole under basic conditions in DMF, although this polymer could not be obtained from the direct polymerization of its corresponding monomer, due to the notorious problem encountered in the chemistry of disubstituted polyacetylenes, namely the deactivation of the transition-metal catalysts for acetylene polymerization by active protons or coordinative ligands in monomers.[3] The detailed synthetic procedure and spectroscopic characterization data are presented in the ESI†. Unlike its parent polymer **P0**, **P1** was nearly insoluble in THF, chloroform and DMF, but exhibited good solubility in alcohol.



Scheme 1 The synthetic route to imidazole-functionalized disubstituted polyacetylene **P1**.

---

[a] *Department of Chemistry, Hubei Key Laboratory on Organic and Polymeric Optoelectronic Materials, Wuhan University, Wuhan, 430072, China. E-mail: lizhen@whu.edu.cn; Fax: +86-27-6875-6757; Tel: +86-27-6225-4108*
[b] *Department of Chemistry, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China*

† Electronic supplementary information (ESI) available: Preparation and characterization details for **P1**; PL spectra of solutions of **P1** at the presence of different ions with different concentrations; PL spectra of films of **P1** after different treatment; UV-Vis spectra of **P0** and **P1**; PL spectra of solutions of the mixture of **P0** and imidazole at the presence of different ions. See DOI: 10.1039/b717764j

There was nearly no difference between the fluorescence intensity of **P1** in the presence and absence of alkali and alkaline earth metal ions; similar phenomena were observed in the cases of Zn^{2+}, Ag^{+}, Mn^{2+}, and Cd^{2+}, due to the poor coordination ability of the imidazole receptor with these ions. Pb^{2+}, Al^{3+} and Cr^{3+} could quench the fluorescence, but not completely. However, Cu^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+} and Ni^{2+} could quench the fluorescence of **P1** more efficiently; in particular, Cu^{2+} could quench the fluorescence completely at very low concentration (1.48 ppm) (Fig. 1 and Fig. S1–S9†), with the Stern–Volmer constant determined to be 3.7×10^{5} M^{-1}. Thus, as demonstrated in Fig. 1, **P1** could act as an efficient chemosensor for the detection of Cu^{2+}, Co^{2+}, Fe^{2+} and Fe^{3+}. The influence of other metal ions to the sensing of Cu^{2+} was also conducted. As shown in the inset in Fig. 1, other metal ions resulted in nearly no disturbance to the selective sensing of **P1** toward Cu^{2+}.

The results described above are very different from those of other conjugated polymers containing imidazole or oligopyridine moieties, indicating that the selective sensing of metal ions by using imidazole groups as receptors can be adjusted by the choice of different conjugated backbones.[9] This is reasonable, since the various degrees of affinity of imidazole moieties toward metal ions should lead to different influences on the interaction between the imidazole groups and the conjugated polymer backbones, due to their different electronic properties. Also, we believe that if other receptors were used instead of imidazole, different sensing behaviours should be observed accordingly. Thus, this piece of work might be just the tip of a huge iceberg of polyacetylene chemosensors. Further work is currently underway in our laboratory.

To test the chemosensing ability of polyacetylene in the presence of the receptors, we measured the fluorescence behaviour of a mixture of **P0** and imidazole in the presence of various metal ions (Fig. S10†). It is easily seen that no metal ions, including Cu^{2+}, could quench the strong fluorescence of **P0**. This indicated that the receptor needed to be linked to the polyacetylene backbone to efficiently transfer the energy from the conjugated backbone to the metal ions. We note that, after attaching the imidazole moieties, although the maximum absorption wavelength of **P1** was nearly unchanged compared to **P0**, its maximum emission wavelength was blue-shifted by 14 nm (Fig. S11†). These phenomena disclosed the minor change of the electronic properties of the conjugated polymers before and after the attachment of the imidazole moieties, partially explaining the totally different sensing behaviour of **P1** and the **P0**–imidazole mixture.

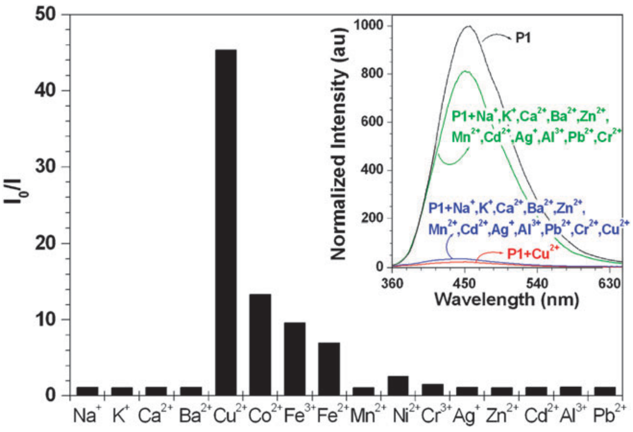
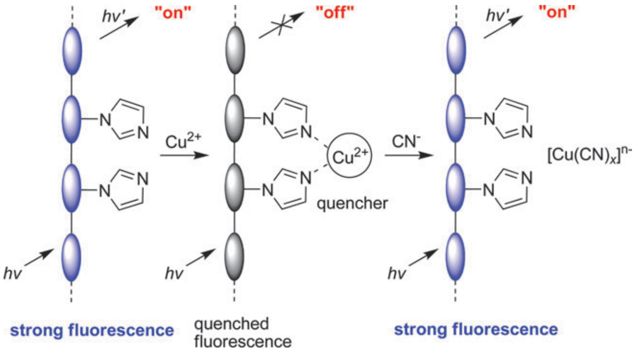


Fig. 1 Fluorescence emission response profiles of **P1**. Inset: Emission quenching of the solution of **P1** in ethanol by Cu^{2+} (1.7 ppm) with and without other metal ions (2.67×10^{-5} M). The polymer concentration was 1.06×10^{-4} M. Excitation wavelength: 335 nm.

The detection of Cu^{2+} by **P1** in the solid state was also investigated (in a similar manner to that reported in the literature),[9c] by dipping the film into aqueous $Cu(NO_3)_2$ solution (Fig. S12†); the strong fluorescence of **P1** was completely quenched. However, the fluorescence recovered after the film was immersed in ammonia solution. This reversibility should benefit the practical application of this polyacetylene chemosensor.

Therefore, the obtained results so far have demonstrated that the strong fluorescence of **P1** could be quenched completely and efficiently by the addition of Cu^{2+}, due to the affinity of imidazole moieties toward Cu^{2+}. If the interaction between the Cu^{2+} ions and the imidazole moieties is then interrupted by some other species, the fluorescence of **P1** might perhaps recover, just like the immersion of the film of the complex of **P1** and Cu^{2+} in ammonia solution. Thus, possibly, we could probe other species based on the fluorescence turn-on of the complex of **P1** and Cu^{2+}. According to this idea, also considering that the new added species should coordinate more easily with Cu^{2+} than imidazole moieties, we thought that CN^{-} might be suitable, due to: (1) the much higher stability constant of the complex of CN^{-} and Cu^{2+} (eqn (S1) and (S2)†);[10] (2) the importance of the detection of CN^{-}, since it is extremely toxic to mammals, and is used industrially in gold mining, electroplating and metallurgy, and could therefore be found in food and plants.[11,12]

The qualitative analysis verified the above thought: addition of CN^{-} turned on the fluorescence of **P1**, as shown in Scheme 2. Encouraged by this result, we studied the recovery behaviour of the fluorescence of the complex of **P1** and Cu^{2+} in detail. As shown in the inset in Fig. 2, the completely quenched fluorescence of **P1** by Cu^{2+} was turned on after the addition of CN^{-}, at concentrations as low as 7.0×10^{-5} M. Further increasing the concentration of CN^{-} led to stronger fluorescence; however, the results were not much better. For example, at a concentration of 2.0×10^{-4} M, the fluorescence intensity was only 1.23 times that when the concentration was 7.0×10^{-5} M (Fig. S13†). However, the fluorescence intensity at 7.0×10^{-5} M was strong enough to



Scheme 2 Schematic representation of Cu^{2+} and CN^{-} sensors based on the fluorescence "turn-off" and "turn-on" of the polyacetylene.

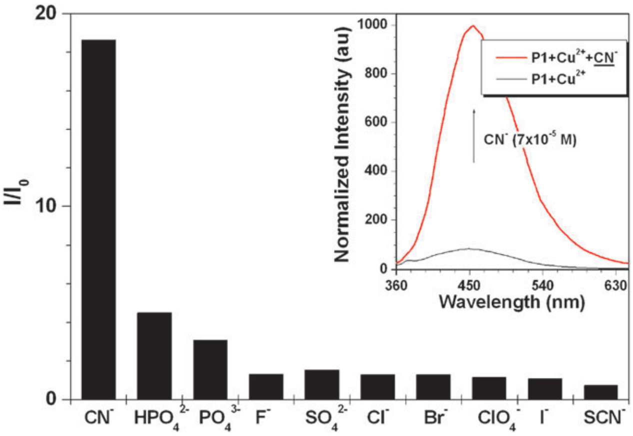


Fig. 2 Fluorescence emission response profiles of **P1** + Cu^{2+}. Inset: Fluorescence emission spectra of **P1** in ethanol after added Cu^{2+}, and after "turning on" by CN^-. The polymer concentration was 0.528×10^{-4} M. Excitation wavelength: 335 nm.

use it as a "turn-on" to probe trace CN^-. Thus, by applying a turn-off–turn-on cycle, **P1** was both a selective chemosensor for Cu^{2+} and a sensitive chemosensor for CN^-.

Also, to evaluate the cyanide-selective nature of **P1**, the influence of other anions was investigated. As shown in Fig. 2 and Fig. S14†, other anions gave nearly no disturbance to the selective sensing of CN^-, except for a little influence from HPO_4^{2-} and PO_4^{3-}. Thus, the selectivity for CN^- over other anions is relatively high.

The detection of CN^- by **P1** in the solid state was also investigated, by first dipping the film into aqueous $Cu(NO_3)_2$ solution to quench the fluorescence, then into aqueous CN^- solution to recover the fluorescence (Fig. S15–16†). Although not so sensitive as the solution, the CN^- concentrations as low as 1.4×10^{-3} M could reverse the quenched fluorescence of **P1**. When the concentration increased to 1.0×10^{-2} M, the fluorescence recovered to nearly the same as that of **P1**.

In summary, we have successfully prepared a new imidazole-functionalized disubstituted polyacetylene by utilizing a postfunctional strategy, and studied its ability to sense metal ions and anions by using its fluorescence spectra. These preliminary results show that:

(1) For the first time, polyacetylenes can act as selective and sensitive chemosensors for metal ions and anions.

(2) After the synthetic challenge of the preparation of disubstituted polyacetylenes bearing polar side chains is resolved, many new polyacetylene-based chemosensors can be conveniently synthesised. The results presented here are just one such example, and thus, a new avenue for promising fluorescent polyacetylene chemosensors might now open up.

(3) The utilization of a metal ion chemosensor to probe anions by an indirect strategy is perhaps a novel idea to develop new chemosensors. Thus, the reported chemosensors for metal ions can also be used to sense trace anions. Otherwise, the anion chemosensors could also be applied to detect metal ions.

We acknowledge the financial support from the National Natural Science Foundation of China (Project Nos. 20402011 and 20674059), the National Basic Research "973" Program, the Research Grants Council of Hong Kong (Project Nos. 602706, 603505 and HKU2/05C), and the Hubei Provincial Government.

Notes and references

1 (*a*) T. Masuda, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**, 165 and references therein; (*b*) C. J. Hawker and K. L. Wooley, *Science*, 2005, **309**, 1200; (*c*) V. Percec, J. G. Rudick, M. Peterca, M. Wagner, M. Obata, C. M. Mitchell, W.-D. Cho, V. S. K. Balagurusamy and P. A. Heiney, *J. Am. Chem. Soc.*, 2005, **127**, 15257; (*d*) K. Okoshi, S. Sakurai, S. Ohsawa, J. Kumaki and E. Yashima, *Angew. Chem., Int. Ed.*, 2006, **45**, 8173; (*e*) T. Aoki and T. Kaneko, *Polym. J.*, 2005, **37**, 717; (*f*) J. Sedlacek and J. Vohlidal, *Collect. Czech. Chem. Commun.*, 2003, **68**, 1745; (*g*) A. P. H. J. Schenning, M. Fransen and E. W. Meijer, *Macromol. Rapid Commun.*, 2002, **23**, 266.

2 (*a*) S. K. Choi, Y. S. Cal, S. H. Jin and H. K. Kim, *Chem. Rev.*, 2000, **100**, 1645; (*b*) E. J. Ginsburg, C. B. Gorman and R. H. Grubbs, in *Modern Acetylene Chemistry*, ed. P. J. Stang and F. Diederich, VCH, Weinheim, 1995, ch. 10; (*c*) R. D'Amato, T. Sone, M. Tabata, Y. Sadahiro, M. V. Russo and A. Furlani, *Macromolecules*, 1998, **31**, 8660; (*d*) K. Akagi, G. Piao, S. Kaneko, K. Sakamaki, H. Shirakawa and M. Kyotani, *Science*, 1998, **282**, 1683; (*e*) R. S. Saunders, R. E. Cohen and R. R. Schrock, *Acta Polym. Sci.*, 1987, **81**, 121; (*f*) S. Koltzenburg, F. Stelzer and O. Nuyken, *Macromol. Chem. Phys.*, 1999, **200**, 821.

3 J. W. Y. Lam and B. Z. Tang, *Acc. Chem. Res.*, 2005, **38**, 745.

4 (*a*) S. W. Thomas, III, G. D. Joly and T. M. Swager, *Chem. Rev.*, 2007, **107**, 1339; (*b*) M. Kimura, T. Horai, K. Hanabusa and H. Shirai, *Adv. Mater.*, 1998, **10**, 459; (*c*) G. Zotti, S. Zecchin, G. Schiavon, A. Berlin and M. Perso, *Chem. Mater.*, 1999, **11**, 3342; (*d*) B. Liu, W. L. Yu, J. Pei, S. Y. Liu, Y. H. Lai and W. Huang, *Macromolecules*, 2001, **34**, 7932; (*e*) H. Tong, L. X. Wang, X. B. Jing and F. S. Wang, *Macromolecules*, 2002, **35**, 7169; (*f*) T. Yasuda, I. Yamaguchi and T. Yamamoto, *Adv. Mater.*, 2003, **15**, 293.

5 Y. Liu, R. C. Mills, J. M. Boncella and K. S. Schanze, *Langmuir*, 2001, **17**, 7452.

6 (*a*) D. T. McQuade, A. E. Pullen and T. M. Swager, *Chem. Rev.*, 2000, **100**, 2537; (*b*) B. Fabre and J. Simonet, *Coord. Chem. Rev.*, 1998, **178–180**, 1211.

7 (*a*) Z. Li, C. Huang, J. Hua, J. Qin, Z. Yang and C. Ye, *Macromolecules*, 2004, **37**, 371; (*b*) Z. Li, J. Qin, S. Li, C. Ye, J. Luo and Y. Cao, *Macromolecules*, 2002, **35**, 9232.

8 (*a*) Z. Li, Y. Dong, A. Qin, J. W. Y. Lam, Y. Dong, W. Yuan, J. Sun, J. Hua, K. S. Wong and B. Z. Tang, *Macromolecules*, 2006, **39**, 467; (*b*) Q. Zeng, Z. Li, Z. Li, C. Ye, J. Qin and B. Z. Tang, *Macromolecules*, 2007, **40**, 5634; (*c*) Z. Li, Q. Li, A. Qin, Y. Dong, J. W. Y. Lam, Y. Dong, C. Ye, J. Qin and B. Z. Tang, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 5672.

9 (*a*) B. Wang and M. R. Wasielewski, *J. Am. Chem. Soc.*, 1997, **119**, 12; (*b*) Y. Zhang, C. B. Murphy and W. E. Jones, *Macromolecules*, 2002, **35**, 630; (*c*) X. Zhou, J. Yan and J. Pei, *Macromolecules*, 2004, **37**, 7078; (*d*) C. Xing, M. Yu, S. Wang, Z. Shi, Y. Li and D. Zhu, *Macromol. Rapid Commun.*, 2007, **28**, 241; (*e*) Z. Q. Gao, G. Binyamin, H. H. Kim, S. C. Barton, Y. C. Zhang and A. Heller, *Angew. Chem., Int. Ed.*, 2002, **41**, 810; (*f*) H. A. Ho and M. Leclerc, *J. Am. Chem. Soc.*, 2003, **125**, 4412.

10 T. Song, J. Xu and G. Cheng, *Inorganic Chemistry*, Higher Education Press, Beijing, 2004.

11 (*a*) Y. K. Yang and J. Tae, *Org. Lett.*, 2006, **8**, 5721 and references therein; (*b*) W. J. Jin, M. T. Fernández-Argüelles, J. M. Costa-Fernández, R. Pereiro and A. Sanz-Medel, *Chem. Commun.*, 2005, 883; (*c*) F. García, J. M. García, B. García-Acosta, R. Martínez-Máñez, F. Sancenón and J. Soto, *Chem. Commun.*, 2005, 2790; (*d*) J. V. Ros-Lis, R. Martínez-Máñez and J. Soto, *Chem. Commun.*, 2005, 5260; (*e*) S. Sun and A. J. Lees, *Chem. Commun.*, 2000, 1687; (*f*) Y. M. Chung, B. Raman, D. S. Kim and K. H. Ahn, *Chem. Commun.*, 2006, 186; (*g*) E. Palomares, M. V. Martínez-díaz, T. Torres and E. Coronado, *Adv. Funct. Mater.*, 2006, **16**, 1166.

12 (*a*) R. Badugu, J. R. Lakowicz and C. D. Geddes, *J. Am. Chem. Soc.*, 2005, **127**, 3635; (*b*) P. Anzenbacher, Jr, D. S. Tyson, K. Jursiková and F. N. Castellano, *J. Am. Chem. Soc.*, 2002, **124**, 6232; (*c*) Y. Zhang, D. Zhang and C. Liu, *J. Phys. Chem. B*, 2006, **110**, 4671; (*d*) H. Liu, X. Shao, M. Jia, X. Jiang, Z. Li and G. Chen, *Tetrahedron*, 2005, **61**, 8095; (*e*) M. Tomasulo, S. Sortino, A. J. P. White and F. M. Raymo, *J. Org. Chem.*, 2006, **71**, 744; (*f*) H. Miyaji and J. L. Sessler, *Angew. Chem., Int. Ed.*, 2001, **40**, 154.