

Click Chemistry Approach to Fluorescence-Based Polybinaphthyls Incorporating a Triazole Moiety for Hg²⁺ Recognition

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Abstract: Optically active polybinaphthyls incorporating triazole moieties were obtained by polymerization of (*R*)-6,6'-dibutyl-3,3'-diethynyl-2,2'-bisoxetoxy-1,1'-binaphthyl and 1,4-diazidobenzene through click reactions. This is the first example of click-generated polybinaphthyls. The responsive optical properties of the polymer upon addition of various metal ions were investigated by fluorescence and UV/Vis spectral studies. The results indicate that the triazole moiety is a receptor that shows excellent fluorescence response for Hg²⁺ recognition without interference from other metal ions.

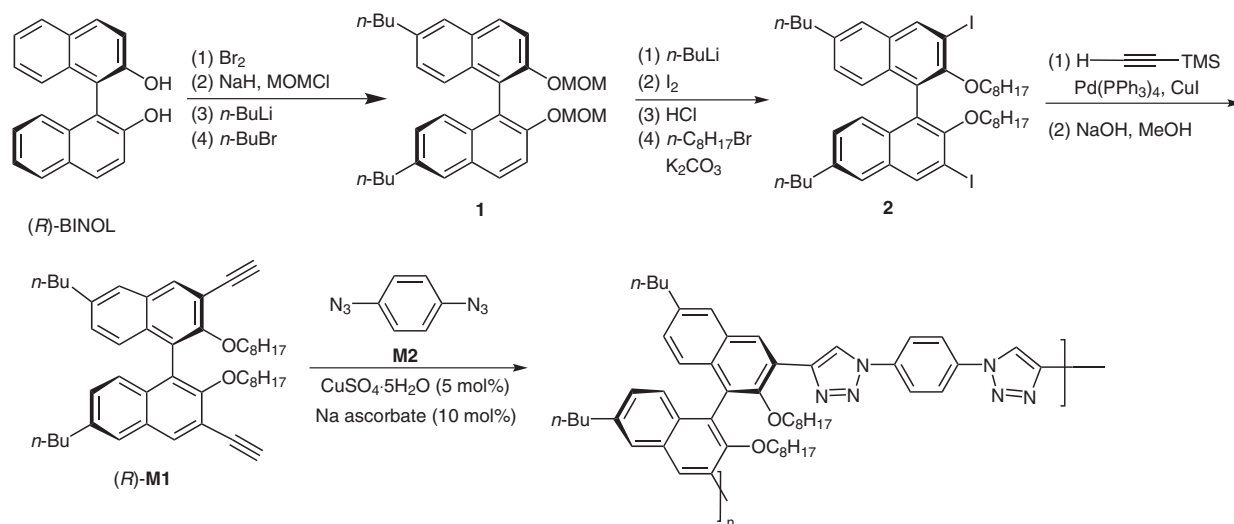
Key words: alkyne-azide cycloaddition, triazole receptors, optically active polybinaphthyls, mercury ion recognition

Chiral conjugated polymers are optically active materials made up of organic fragments such as aromatic rings and unsaturated carbon or heteroatom bonds with delocalizable π -electronic systems. Chiral binaphthol (BINOL) and its derivatives are important C₂ symmetric compounds, and the skeletal structure of BINOL at the 3,3'- or 6,6'-positions of binaphthyl can be selectively functionalized on a well-defined molecular level that can lead to a variety of binaphthyl derivatives. Conjugated polymers incorporating an optically active binaphthyl moiety in the main chain can exhibit excellent fluorescence, with good quantum efficiencies due to the extended π -electronic structure.¹ Recently, we have initiated a project on fluorescence-based polybinaphthyls.^{1c,d} These polybinaphthyls exhibit highly sensitive and selective behavior that can be used to detect metal ions by the introduction of appropriate receptors for specific analytes. Since mercury and its derivatives are deleterious for human health and the environment, the detection of mercury in environmental or biological systems has gained tremendous attention in recent years.² However, to our knowledge, there is no report on polybinaphthyls containing a triazole moiety for mercury detection through click reactions.

Due to the high efficiency and technical simplicity, click reactions have been used extensively in synthetic chemistry and the preparation of novel materials. The exemplary click reaction is the copper(I)-catalyzed Huisgen [3+2] dipolar cycloaddition (CuAAC) between an alkyne and an azide, described by Kolb, Finn, and Sharpless.³ Polymer chemists have employed click chemistry to construct den-

dritic compounds,⁴ nonlinear optics,⁵ and linear macromolecules.⁶ Functionalization and stabilization of nanoparticles represents another arena with rich opportunities for click chemistry. Li and Benicewicz grew an azido-functional methacrylate polymer through surface-initiated RAFT polymerization on silica particles.⁷ Rather surprisingly, very few click-generated molecules as fluorescence sensors for metal ion detection have been reported.⁸ Todd and Watkinson reported a cyclam-based sensor which was the first example of a triazole unit functioning as a coordinating ligand for Zn²⁺ detection.^{8a} As such, there are only a few reports on the synthesis of π -conjugated polymers through 1,3-cycloaddition.⁹ In this paper we report for the first time the synthesis of optically active polybinaphthyls incorporating a triazole moiety for mercury recognition through a click reaction. Compared with other cations (K⁺, Mg²⁺, Pb²⁺, Co²⁺, Ni²⁺, Cd²⁺, Cu²⁺, Zn²⁺ and Pd²⁺), Hg²⁺ leads to nearly complete fluorescence quenching of this polymer. Such distinct ion-responsive behavior revealed that the fluorescence sensor was generated as a result of triazole formation (click reaction), rather than simply bringing the sensor and reporter units together through a triazole linkage. The results indicate this kind of chiral polybinaphthyl incorporating a triazole moiety as a receptor, exhibits high sensitivity and selectivity for Hg²⁺ recognition without interference from other metal ions.

The synthesis of the monomer (*R*)-**M1** and the chiral polymer are outlined in Scheme 1. The monomer 1,4-diazidobenzene (**M2**), could be synthesized from *p*-phenylenediamine by a two-step reaction according to reported literature.¹⁰ (*R*)-6,6'-Dibutyl-3,3'-diethynyl-2,2'-bisoxetoxy-1,1'-binaphthyl [(*R*)-**M1**] can be obtained by an eight-step reaction from the starting material (*R*)-BINOL.¹¹ In this paper, typical CuAAC reaction conditions were applied to the synthesis of the chiral polybinaphthyls.¹² The polymerization could be carried out under mild reaction conditions in aqueous solution, in the presence of a catalytic amount of sodium ascorbate and CuSO₄·5H₂O, with yields as high as 85%. The number-average molecular weight (*M_n*) and the weight-average molecular weight (*M_w*) of the polymer were 9550 and 15450, respectively, with a polydispersity index of 1.6 (see the Supporting Information). Unlike the usually poor solubility of click polymers,¹³ the resulting polymer showed moderate solubility in common solvents such as toluene, THF, CHCl₃, and CH₂Cl₂, which could be attributed to the nonplanarity of the twisted polymer in the



Scheme 1 Synthesis of the chiral polymer ligand

main-chain backbone and the flexible octoxy or *n*-butyl substituents on the binaphthyl units as side chains of the polymer. According to a thermal analysis of the polymer (see the Supporting Information), it has a high thermal stability without loss of weight below 280 °C, which provides desirable thermal properties for practical application as a fluorescence sensor.

As shown in Figure 1, this polymer has two absorption bands at 262 and 308 nm. The Hg^{2+} sensing properties of the polymer were studied in CHCl_3 solution with a polymer concentration of $1.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$. Upon addition of Hg^{2+} in MeCN, the absorption features of the polymer changed greatly. The absorption peaks of the polymer at 262 nm and 308 nm decreased as shown in Figure 1, which can be attributed to the reduction of the π -conjugated system induced by the coordination of the triazole unit with Hg^{2+} .¹³

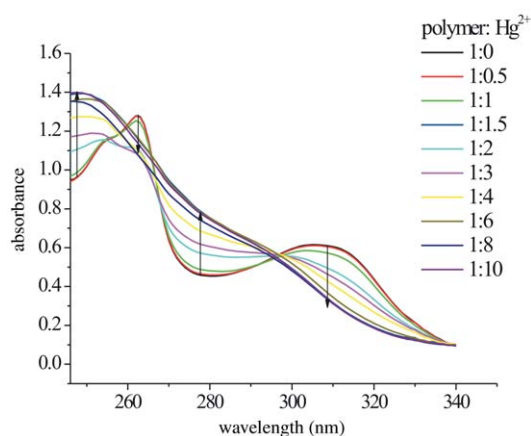


Figure 1 Absorption spectra of the polymer ($1.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ in CHCl_3) in the presence of various molar ratios of Hg^{2+} in MeCN

The fluorescent wavelength of the polymer appeared at 382 nm upon excitation at 312 nm, and the photoluminescence efficiency (Φ_{PL}) of the polymer was 0.44. The effect

of the fluorescence response behavior of the chiral polymer in the presence of Hg^{2+} was investigated. As is evident from Figure 2, strong fluorescence quenching could be detected upon the addition of Hg^{2+} , with nearly complete quenching at a polymer/metal molar ratio of 1:4, which could be attributed to the intramolecular photoinduced charge-transfer between the polymer backbone and the binding metal complex.

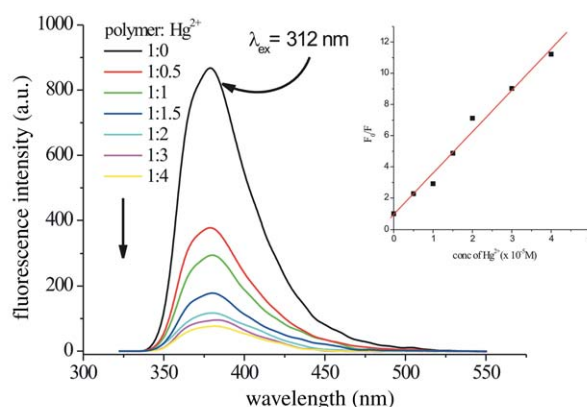


Figure 2 Fluorescence response of polymer ($1.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ in toluene) in the presence of various molar ratios of Hg^{2+} in MeCN; inset: Stern–Volmer plot of the polymer

The fluorescence quenching efficiency was related to the Stern–Volmer constant (K_{sv}), which was determined by monitoring changes of the fluorescence intensity and applying the measured values to the Stern–Volmer equation: $F_0/F = 1 + K_{\text{sv}}[Q]$, where F_0 is the fluorescence intensity in the absence of the quencher, F is the fluorescence intensity in the presence of the quencher, and $[Q]$ is the quencher concentration.^{2c,14} At concentrations of Hg^{2+} ranging from 0 to $4.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$, a linear Stern–Volmer plot was obtained with a K_{sv} value of $2.67 \times 10^5 \text{ M}^{-1}$. Since dynamic quenching processes would be expected to give a straight line with a y-intercept of 1, we may conclude that

the mechanism of the quenching process involves collisional deactivation.¹⁵

The fluorescence response behavior of the polymer in the presence of other metal ions was examined under the same conditions as for the detection of Hg²⁺ described above. The addition of K⁺, Mg²⁺, Pb²⁺, Co²⁺, Ni²⁺, Cd²⁺, Cu²⁺ and Zn²⁺ caused only slight fluorescence quenching of the polymer even at high concentrations of metal ions (Figure 3). In addition, an obvious fluorescence quenching response of the polymer was observed upon addition of Pd²⁺, however, the fluorescence quenching ratio was much lower than that induced by Hg²⁺. The degree of fluorescence quenching of the polymer upon addition of Pd²⁺ reached its maximum (25%) at a Pd²⁺ concentration of 1.0×10^{-4} mol·L⁻¹. The results indicate that the chiral polymer exhibited excellent selectivity for Hg²⁺ recognition.

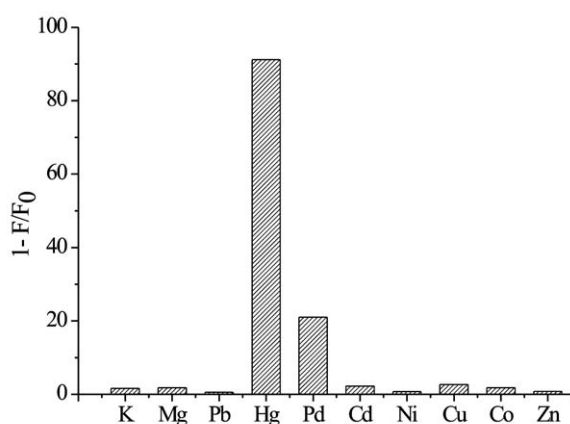


Figure 3 Fluorescence quenching ratios of the polymer (1.0×10^{-5} mol·L⁻¹ in toluene) in the presence of various metal ions (4.0×10^{-5} mol·L⁻¹)

Normally, an excellent fluorescence sensor with highly sensitive and selective properties should suffer only minor or, ideally, no interference from other metal ions. We therefore checked the Hg²⁺ recognition sensitivity for interference by other metal ions; the recognition experiments were conducted with Hg²⁺-polymer solutions in the presence of equimolar amounts (4.0×10^{-5} mol·L⁻¹) of K⁺, Mg²⁺, Pb²⁺, Co²⁺, Ni²⁺, Cd²⁺, Cu²⁺, Zn²⁺ or Pd²⁺ (Figure 4). The deviation in the fluorescence quenching caused by the interference of other metal ions was less than 10%. The results indicated that the presence of other cations did not interfere with the Hg²⁺ detection. The unique selectivity and high sensitivity of the polymer for Hg²⁺ recognition can be attributed to several factors, such as the structural rigidity of the triazole unit, the larger radius of the Hg²⁺ ion, its soft acid property, and the binding ability of the triazole unit with Hg²⁺.^{14a}

In summary, a chiral polymer was synthesized by a click reaction under mild reaction conditions in aqueous solution. The responsive optical properties of the polymer upon addition of various metal ions were investigated. Compared with other cations (K⁺, Mg²⁺, Pb²⁺, Co²⁺, Ni²⁺,

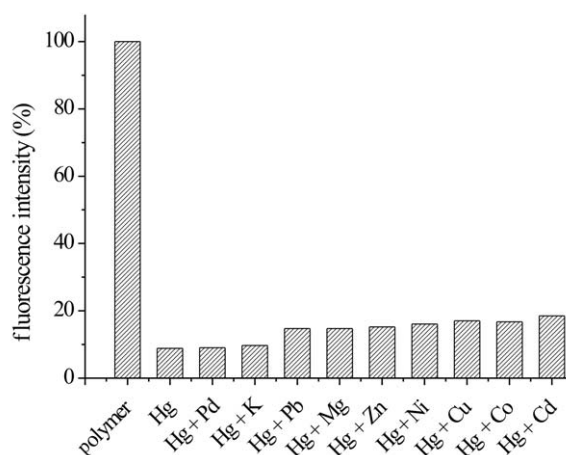


Figure 4 The fluorescence intensity change profiles of the polymer (1.0×10^{-5} mol·L⁻¹ in toluene) with selected metal ions (4.0×10^{-5} mol·L⁻¹) in the presence of Hg²⁺ (4.0×10^{-5} mol·L⁻¹)

Cd²⁺, Cu²⁺, Zn²⁺ and Pd²⁺), Hg²⁺ led to nearly complete fluorescence quenching of this polymer. The material also exhibited an excellent fluorescence response for Hg²⁺ recognition without interference from other metal ions. The results indicate that chiral polybinaphthyl incorporating triazole units can serve as sensitive and selective Hg²⁺ recognition receptors.

Supporting Information for this article is available online at <http://www.thieme-connect.com/ejournals/toc/synlett>.

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References and Notes

- (1) (a) Pu, L. *Chem. Rev.* **2004**, *104*, 1687. (b) Pu, L. *Chem. Rev.* **1998**, *98*, 2405. (c) Liu, Y.; Zhang, S.; Miao, Q.; Zheng, L.; Zong, L.; Cheng, Y. *Macromolecules* **2007**, *40*, 4839. (d) Liu, Y.; Zong, L.; Zheng, L.; Wu, L.; Cheng, Y. *Polymer* **2007**, *48*, 6799. (e) Deussen, H. J.; Hendrickx, E.; Boutton, C.; Krog, D.; Clays, K.; Bechgaard, K.; Persoons, A.; Bjørnholm, T. *J. Am. Chem. Soc.* **1996**, *118*, 6841. (f) Koeckelberghs, G.; Verbiest, T.; Vangheluwe, M.; De Groof, L.; Asselberghs, I.; Picard, I.; Clays, K.; Persoons, A.; Samyn, C. *Chem. Mater.* **2005**, *17*, 118. (g) Li, Z. B.; Pu, L. *J. Mater. Chem.* **2005**, *15*, 2860.
- (2) (a) Zhang, Z.; Wu, D.; Guo, X.; Qian, X.; Lu, Z.; Zu, Q.; Yang, Y.; Duan, L.; He, Y.; Feng, Z. *Chem. Res. Toxicol.* **2005**, *18*, 1814. (b) Nolan, E. M.; Lippard, S. J. *Chem. Rev.* **2008**, *108*, 3443. (c) Kim, I. B.; Dunkhorst, A.; Gilbert, J.; Bunz, U. H. F. *Macromolecules* **2005**, *38*, 4560. (d) Fan, L. J.; Jones, W. E. *J. Am. Chem. Soc.* **2006**, *128*, 6784. (e) Liu, S. J.; Fang, C.; Zhao, Q.; Fan, Q. L.; Huang, W. *Macromol. Rapid Commun.* **2008**, *29*, 1212.
- (3) (a) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem. Int. Ed.* **2002**, *41*, 2596. (b) Tornøe, C. W.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057.

- (4) (a) Malkoch, M.; Schleicher, K.; Drockenmüller, E.; Hawker, C. J.; Russell, T. P.; Wu, P.; Fokin, V. V. *Macromolecules* **2005**, *38*, 3663. (b) Lee, J. W.; Kim, J. H.; Han, S. C.; Shin, W. S.; Jin, S. H. *Macromolecules* **2006**, *39*, 2418.
- (5) Zeng, Q.; Li, Z.; Li, Z.; Ye, C.; Qin, J.; Tang, B. Z. *Macromolecules* **2007**, *40*, 5634.
- (6) (a) Tsarevsky, N. V.; Sumerlin, B. S.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 3558. (b) Gao, H. F.; Matyjaszewski, K. *Macromolecules* **2006**, *39*, 4960.
- (7) Li, Y.; Benicewicz, B. C. *Macromolecules* **2008**, *41*, 7986.
- (8) (a) Tamanini, E.; Katewa, A.; Sedger, L. M.; Todd, M. H.; Watkinson, M. *Inorg. Chem.* **2009**, *48*, 319. (b) Varazo, K.; Xie, F.; Gullledge, D.; Wang, Q. *Tetrahedron Lett.* **2008**, *49*, 5293. (c) Varazo, K.; Le Droumaguet, C.; Fullard, K.; UWang, Q. U. *Tetrahedron Lett.* **2009**, *50*, 7032. (d) Zhu, L.; Lynch, V. M.; Anslyn, E. V. *Tetrahedron* **2004**, *60*, 7267.
- (9) (a) Bakbak, S.; Leech, P. J.; Carson, B. E.; Saxena, S.; King, W. P.; Bunz, U. H. F. *Macromolecules* **2006**, *39*, 6793. (b) Van Steenis, D. J. V. C.; David, O. R. P.; Van Strijdonck, G. P. F.; Van Maarseveen, J. H.; Reek, J. N. H. *Chem. Commun.* **2005**, 4333.
- (10) Minato, M.; Lahti, P. M. *J. Am. Chem. Soc.* **1997**, *119*, 2187.
- (11) Huang, X.; Xu, Y.; Miao, Q.; Zong, L.; Hu, H.; Cheng, Y. *Polymer* **2009**, *50*, 2793.
- (12) Procedure for the synthesis of chiral polymer, see:
(a) Morten, M. *Macromol. Rapid Commun.* **2008**, *29*, 12.
(b) A mixture of (*R*)-**M1** (270.0 mg, 0.40 mmol), **M2** (64.0 mg, 0.40 mmol), sodium ascorbate (10 mol%, 7.9 mg, 0.04 mmol) and CuSO₄·5H₂O (5 mol%, 5.0 mg, 0.02 mmol) were dissolved in a mixture of THF (15 mL) and H₂O (15 mL). The solution was stirred at r.t. for 2 d under an N₂ atmosphere. The resulting polymer was filtered and washed with diluted ammonia water, H₂O and methanol several times. Further purification could be achieved by dissolving the polymer in THF and precipitating in methanol again. The polymer was dried in vacuum to give the product as a yellow solid (282.6 mg, 85.0% yield). Polymer spectroscopic data: [α]_D²⁵ −483.9 (c 0.0083, THF); ¹H NMR (300 Hz, CDCl₃): δ = 8.95 (br, 2 H), 8.72 (br, 2 H), 8.04 (br, 4 H), 7.82 (br, 2 H), 7.18 (br, 4 H), 3.68–3.64 (m, 2 H), 3.32–3.30 (m, 2 H), 2.80–2.76 (m, 4 H), 1.75–1.66 (m, 4 H), 1.46–1.39 (m, 4 H), 1.23–0.73 (m, 36 H). FT-IR (KBr): 3442, 3062, 2953, 2923, 2853, 1606, 1523, 1496, 1462, 1453, 1377, 1352, 1328, 1231, 1035, 1024 cm^{−1}. Anal. Calcd for (C₅₄H₆₇N₆O₂)_n: C, 77.94; H, 8.12; N, 10.10. Found: C, 78.01; H, 8.04; N, 10.02.
- (13) Karim, M. A.; Cho, Y. R.; Park, J. S.; Kim, S. C.; Kim, H. J.; Lee, J. W.; Gal, Y. S.; Jin, S. H. *Chem. Commun.* **2008**, 1929.
- (14) (a) Zou, Y.; Wan, M.; Sang, G.; Ye, M.; Li, Y. *Adv. Funct. Mater.* **2008**, *18*, 2724. (b) Murphy, C. B.; Zhang, Y.; Troxler, T.; Jones, W. E. *J. Phys. Chem. B* **2004**, *108*, 1537.
- (15) Zhang, Y.; Murphy, C. B.; Jones, W. E. *Macromolecules* **2002**, *35*, 630.