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A novel chemosensor-bipyridyl end capped hyperbranched conjugated polymer

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Abstract

A novel hyperbranched conjugated chemosensor with bipyridyl groups as periphery groups (BPY-HPV) was synthesized. BPY-HPV was highly sensitive to metal ions (Cu^{2+}, Ni^{2+}) for the strong coordination interaction (K_{sv} at the order of 10^7 mol^{-1} L) monitored by fluorescence spectroscopy. Moreover, by hydrogen bonds and charge transfer interaction, BPY-HPV shows strong interaction with 1,1,2,2-tetrachloroethane whatever in CH_2Cl_2 ($K_{sv} \sim 10^6$ mol^{-1} L) or film.

Keywords: Hyperbranched conjugated polymer; Hydrogen bonding; Fluorescence; Tetrachloroethane

Conjugated polymers are superior to its organic counterparts in their collective and amplifying response, ease to make devices and so on. A variety of molecular recognition events based on conjugated polymers have been revealed by switching or tuning the luminescence of the nearby signaling moieties based charge transfer, photoinduced electron transfer or electronic-energy transfer [1–4]. The conjugated polymers designed for recognition are focused on those with linear rigid rod structure, such as PPP, PPV and PPE [5,6]. Several linear copolymers of bipyridyl groups, a kind of effective functional group for ion recognition, and phenylene vinylene or fluorine moieties were reported to have high metal ion selectivity. Hyperbranched polymer, a kind of polymer of high solubility and thermal stability, is characteristic of global structure, and the end groups were exposed on the surface of the globe [7,8]. So if bipyridyl groups were incorporated into the periphery groups of the fluorescent hyperbranched polymer, they would contact with the environment directly. The high density of end groups will endow this polymer to be high effective and selective for ion or molecular recognition.

Here we report synthesis, characterization of one bipyridyl end-capped hyperbranched phenylene vinylene (BPY-HPV). The interaction between BPY-HPV and metal ions or 1,1-2,2-tetrachloroethane (TCE) in CH_2Cl_2 solution was investigated. Also the switching behavior in film was studied. The chemical structure of BPY-HPV is given in Scheme 1.

To a solution of benzene-1,3,5-trialdehyde 0.3 g (1.85 mmol) and [2,5-dimethoxy-1,4-xylylene]bis(triphenylphosphonium chloride 1.4 g (1.85 mmol) in DMF 15 mL was dropped a solution of CH_3OK (3.7 mmol) in CH_3OH under vigorously stirring and a dynamic nitrogen atmosphere at room temperature. After 6 h, 5′-methylbipyridyl monoylid 0.97 g (1.85 mmol) was added followed by the addition of CH_3OK 0.13 g (1.85 mmol) in CH_3OH under

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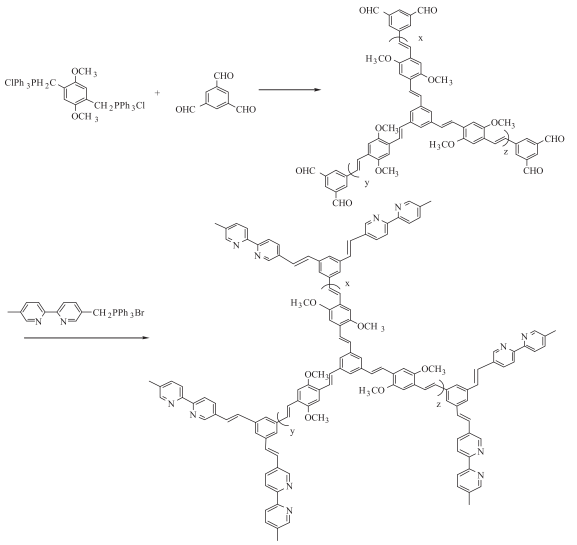


Scheme 1. The synthetic method and chemical structure of BPY-HPV.

vigorously stirring. The reaction was kept at room temperature for 6 h. Then the polymer could be precipitated from methanol followed by extracting with methanol for two days. The resulting polymer was obtained as a bright-yellow solid with an overall yield 45%.

FTIR (KBr pellet, cm^{-1}): 3006 (Ar–H, =C–H, w), 2929 (CH_3, w), 1590, 1542, 1496, 1462, 1407, 1208 (ν_{as} = C–O–C, s), 1042 (ν_s = C–O–C, s), 964 (δ = C–H, trans, ms), 888 (w), 864 (w), 823 (w), 697 (δ = CH, cis vw).

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.3 (CH_3-, S), 3.2 (s, CH_3O–), 3.8 (s, CH_3O–), 6.4–7.8 (m, –Ar –H), 8.1–8.8 (m, bipyridyl-H);^{13}C NMR (400 MHz, $CDCl_3$): δ 21.09 (CH_3-), 56.04 (CH_3O–), 108.94, 112.89, 118.08, 121.34–129.16, 133.04–133.8, 145.78, 148.04–151.35 (aromatic carbon on double bond and phenyl rings), 155.63–156.60 (aromatic carbon on bipyridyl groups); calcd. For $(C_{17}H_{15}O_2N)_n$ $(265)_n$, (%) C 76.9, H 5.66, O 12.07, N 5.28; found (%) C 78.56, H 5.55, O 10.59, N 5.30; MALDI-TOF (MS): 3051, 2952, 2295, 1651, and 1398.

FTIR, ^{1}H NMR and ^{13}C NMR and elemental analysis results were consistent with the proposed molecular structures. From both ^{1}H NMR and ^{13}C NMR, the proton signal at 2.3 and 21 ppm could be attributed to methyl groups on the bipyridyl groups, which could be clearly discerned from the signal of methoxy groups on the distylrylbenzene units. Also, the signal of bipyridyl groups could be found at 8.1–8.8 ppm and 155–156 ppm different from the signal of phenyl and vinylene double bonds, which could be further confirmed by elemental analysis with a percentage of nitrogen at 5.3%. MALDI–TOF was used to determine the molecular weight of the polymer, since GPC for its linear standard (polystyrene) is not suitable for the determination of a polymer with a hyperbranched structure.

The main absorption peak of BPY-HPV in CH_2Cl_2 is located in 323 nm and 395 nm corresponding to the stilben and distyrylbenzene units. The main emission peak located at 455 nm with a shoulder at about 480 nm corresponding to the emission of distyrylbenzene units [8]. Thus in BPY-HPV, the periphery units act as the light-harvesting antenna, which funnel the energy to the distyrylbenzene units, then it emits from the low energy of distyrylbenzene moieties. The energy transfer could be supported by investigation of the lifetime of BPY-HPV in CH_2Cl_2, The decay curve exhibited biexponential fitting with a major fast-decay component (1.33 ns (65.41%)) along with a slow decay component (2.58 ns (34.56%)).

The fluorescence of BPY-HPV in CH_2Cl_2 could be quenched significantly by the addition of increasing amounts of metal ions, such as nickel, copper, *etc*. The quenching behavior of the emission peak maximum obeys Stern–Volmer equation, namely, $F_0/F = 1+K_{sv}[C_M]$. Where F_0 is the fluorescence intensity in the absence of metal perchlorate salt, F is the intensity of fluorescence in the presence of metal ions; K_{sv} is the Stern–Volmer quenching constant and C_M is the concentration of metal ions. The quenching constant was determined to be 1.6×10^7 mol^{-1} L and 1.1×10^7 mol^{-1} L for copper and nickel ions respectively (see Fig. 1). For Ag^+, the K_{sv} is 4.4×10^4 mol^{-1} L. The strong interaction and high selectivity may arise from the well-matched size between copper ions and bipyridyl groups. And the strong coordination interaction will change the electron density and conformation of bipyridyl groups, then the electron or energy transfer between bipyridyl–metal ion complex and distyrylbenzene moieties would result

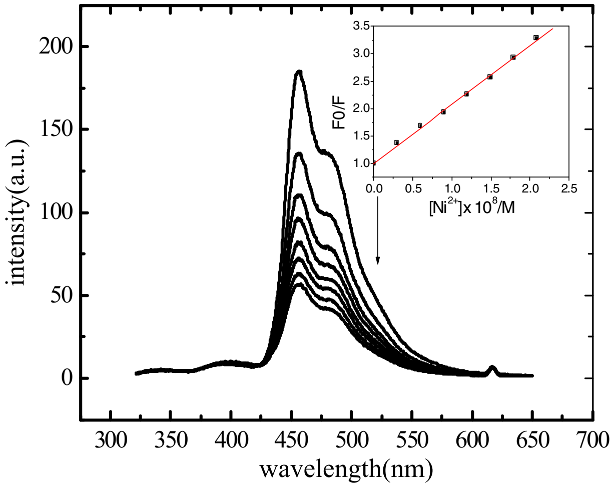


Fig. 1. Fluorescence quenching of BPY-HPV by $Cu(ClO_4)_2$ with the excitation wavelength at 320 nm and the concentrations of Cu^{2+} are 0, 2.96×10^{-8}, 6×10^{-8}, 8.96×10^{-8}, 1.19×10^{-7}, 1.49×10^{-7}, 1.79×10^{-7}, 2.08×10^{-7} mol L^{-1} and BPY-HPV is 1.5×10^{-2} mg/mL respectively. The inset is the corresponding Stern–Volmer curve.

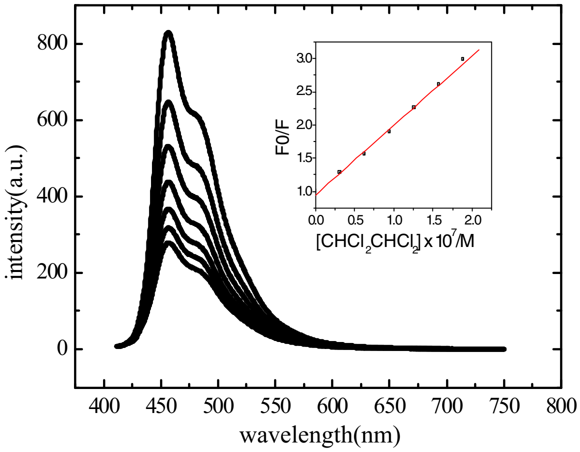
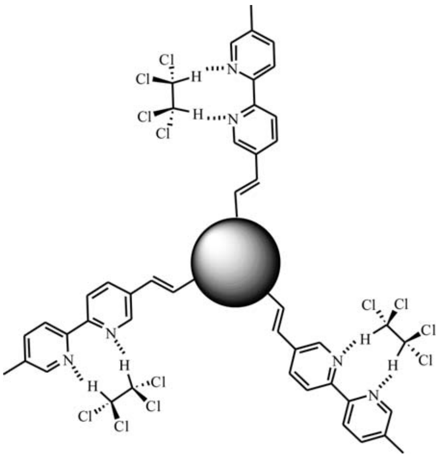


Fig. 2. Fluorescence quenching of BPY-HPV by TCE, the concentrations of TCE are 0, 5×10^{-8}, 1×10^{-7}, 1.5×10^{-7}, 2.0×10^{-7}, 2.5×10^{-7}, 3.0×10^{-7} mol L^{-1} respectively, and BPY-HPV is 1.5×10^{-2} mg/mL. The inset is the corresponding Stern–Volmer curve.



Scheme 2. The proposed interaction mode between BPY-HPV and 1,1,2,2-tetrachloroethane.

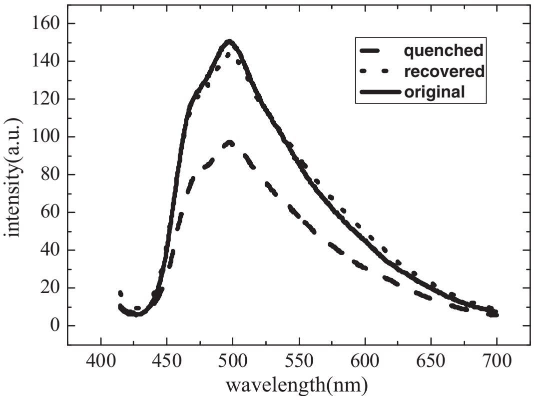


Fig. 3. Fluorescence spectra of BPY-HPV before (solid line) and after being exposed to TCE solution (dashed line) and TEA (dotted line) vapor.

in the fluorescence quenching of BPY-HPV^3, which is contrast to the conjugation length change for its linear counterpart arising from metal-complexation induced conformation change [2].

Moreover, the emission of BPY-HPV could also be quenched greatly (K_{sv} 6×10^6 mol^{-1} L) (see Fig. 2) by TCE. The quenching behavior also obeys Stern–Volmer equation. Considering the chemical structure of TCE, the electron-withdrawing effect of the chloride atoms will make the hydrogen atom act as naked protons. The two protons may interact with nitrogen atom of the bipyridyl groups by a hydrogen bonding-like interaction. Also because the electron-accepting ability of the four chlorine atoms, charge transfer interaction may happen between polymer and TCE through hydrogen atoms, which could be partly supported by the interaction between BPY-HPV and glycol, since glycol could also be expected to have a stronger hydrogen bonds forming ability, which the quenching constant is very low (K_{sv} 3.28 mol^{-1} L). So the interaction may be a cooperative mode of hydrogen bonding and charge transfer. The proposed interactive mode between BPY-HPV and TCE was given in Scheme 2.

Compared with the strong fluorescence of the film spin-coated from a solution in CH_2Cl_2, the fluorescence of that with TCE as solvent was quenched completely. And while the spin-coated film from CH_2Cl_2 solution was dipped into a solution of TCE in cyclohexane (10^{-3} mol L^{-1}), the fluorescence of BPY-HPV was quenched gradually with increasing of the time. But when the film was dipped into triethylamine, the fluorescence could be completely recovered as shown in Fig. 3. Thus, a chemosensory device based on BPY-HPV could be realized.

To our knowledge, this is the first example of chemosensory based on hyperbranched conjugated polymers containing bipyridyl groups on the periphery positions. It shows high sensitivity to metal ions and 1,1,2,2-tetracholoethane by coordination or hydrogen bonding interaction.

Acknowledgments

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References

[1] J. Wang, D. Wang, E.K. Miller, et al. Macrolmolecules 33 (2000) 5152.
[2] B. Wang, M. Wasielewski, J. Am. Chem. Soc. 119 (1997) 1221.
[3] M. Kimura, T. Horai, K. Hanabusa, et al. Adv. Mater. 10 (1998) 459.
[4] (a) K.D. Ley, K.S. Schanze, J. Am. Chem. Soc. 119 (1997) 3423;
(b) K.A. Walters, K.D. Ley, K.S. Schanze, Chem. Commun. (1998) 1115.
[5] (a) D.T. McQuade, A.E. Pullen, T.M. Swager, Chem. Rev. 2537 (2000) 100;
(b) S.W. Thomas III, G.D. Joly, T.M. Swager, Chem. Rev. 107 (2007) 1339.
[6] A.P. de Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, et al. Chem. Rev. 97 (1997) 1515.
[7] Q. He, H. Huang, F. Bai, et al. Macromol. Rapid Commun. 27 (2006) 302.
[8] Q. He, F. Bai, J. Yang, et al. Thin Solid Film 417 (2002) 183.