

A New Conjugated Polymer Chemosensor Functionalised with 2,6-Bis(1,3,4-oxadiazole-2-yl)pyridine for Metal Ion Recognition

Nam Choul Yang, Jae Kyun Jeong, and Dong Hack Suh*
*School of Chemical Engineering, College of Engineering, Hanyang University,
 17 Haengdang 1-dong, Seongdong-gu, Seoul 133-791, Korea*

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A new conjugated alternative copolymer based on 2,6-bis(1,3,4-oxadiazol-2-yl)pyridine and 9,9-dialkylfluorene in a main chain showed strong blue fluorescence with band maxima at 389 nm and 405 nm in the 1,2-dichloroethane solution and possessed sensitivity to various metal ions such as Ni²⁺ and Fe³⁺ as a fluorescence-mode chemosensor.

Chemosensors based on conjugated polymers recently have attracted considerable interests due to their some merits over the sensor systems based on small molecules in the enhanced sensitivity, many transduction methods and facile processibility for condensed phase applications.^{1,2} The semiconductive molecular structure formed along the conjugated polymer chain provides transductional amplification and various transduction signals such as optical absorption, fluorescence and electrical conductivity.^{1,2}

The conjugated polymers functionalized with electron-donor groups such as crown ethers, aza crown ethers and calixarenes as side chains for sensing metal ions have been the most dominantly-studied sensory systems. However, these conjugated polymers are adequate to recognize small size alkali metal ions such as Li⁺, Na⁺, and K⁺.¹ To be sensitive to various metal ions including transition metal ions, a 2,2'-bipyridyl group, one of well-known bidentate ligands, has been employed in the main chain of conjugated polymers.³⁻⁶ Recently, oligomeric poly(*p*-phenylenevinylene) with a terpyridyl side chain sensitive to transition metal ions has been reported.⁷ To our knowledge, these type of conjugated polymers sensitive to metal ions are still rare.

In this letter, we describe the synthesis and characterization of a new conjugated polymer alternatively having 9,9-didodecylfluorene and 2,6-bis(1,3,4-oxadiazol-2-yl)pyridine designed as a terpyridine analogue appropriate to metal ion recognition.

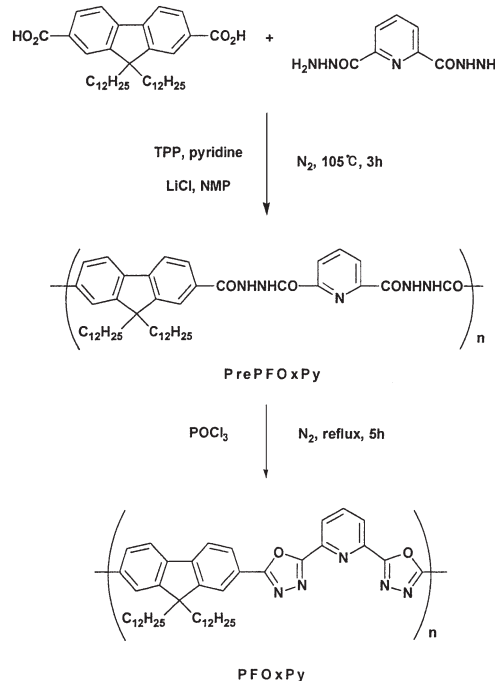
The conjugated polymer PFOxPy is prepared via a polyhydrazide precursor PrePFOxPy. This synthetic route was chosen to exclude the possibility of introduction of metal ions during preparation of the polymer to the utmost. The white fibrous polyhydrazide PrePFOxPy was polymerized from 9,9'-didodecylfluorene-2,7-dicarboxylic acid and pyridine-2,6-dicarboxylic acid dihydrazide by a Yamazaki-Higashi phosphorylation polyamidation.⁸ Dehydrocyclization of PrePFOxPy using POCl₃ as both a dehydrating agent and a reaction solvent resulted in the polyoxadiazole PFOxPy as light gray fibrous powder.⁹ Determined by IR and NMR spectra, the conversion from PrePFOxPy¹¹ to PFOxPy¹² was found to be complete. The yield of PrePFOxPy and PFOxPy was 99% and 95%.

Most polyoxadiazoles showed poor solubility in common organic solvents due to the chain rigidity from a heterocyclic group. However, PFOxPy was very soluble in some common

organic solvents such as tetrahydrofuran, 1,4-dioxane, chlorobenzene and chlorinated hydrocarbons such as chloroform and 1,2-dichloroethane (DCE) due to the increase of solubility by introducing long alkyl chains in a fluorene group and the *m*-linkage in a pyridine group to kink the rigid main chain.⁶ Measured by gel permeation chromatography (GPC) with tetrahydrofuran as an eluent, the weight-average and number-average molecular weights of PFOxPy were 3.3×10^4 and 1.6×10^4 , respectively.

PFOxPy in the DCE solution showed symmetrical UV-visible absorption and fluorescence spectra with fine vibrational structures. UV-visible absorption and fluorescence maxima of PFOxPy were 352 and 372 nm and 389 and 405 nm, respectively, so this polymer showed deep blue fluorescence to human eyes. Determined by comparison with 9,10-diphenylanthracene (fluorescence quantum efficiency = 0.90 in cyclohexane excited at 350 nm), the fluorescence quantum efficiency of PFOxPy was relatively high (0.46), which provided good applicability to a fluorescent chemosensor.

The metal ion recognition property of PFOxPy was monitored in 1×10^{-5} M (based on a repeating unit) DCE by UV-visible absorption and fluorescence spectroscopies. Metal ions (Hg²⁺, Al³⁺, Fe³⁺, Ni²⁺, Mn²⁺, Co²⁺, Cu²⁺, Pb²⁺, and Zn²⁺)



Scheme 1. Synthetic scheme of PFOxPy.

were prepared from their acetate or chloride salts dissolved in methanol.

The UV-visible absorption spectrum of PFOxPy did not change remarkably with the addition of any metal ion applicants, but near 400 nm, there was a weak increasing of the absorption peak. So it seems that the polymer PFOxPy interact weakly with metal ion applicants by metal to ligand charge transfer.¹⁰ This result showed a different tendency in comparison with those of 2,2'-bipyridyl-based conjugated polymers exhibiting conformation changes of planarization of a bipyridyl group by introducing metal ions.³

Figure 1 shows the fluorescence spectra change of PFOxPy with the concentration of Ni²⁺. Contrary to UV-visible spectra, the addition of a metal ion led to the change of fluorescence intensity. In all cases, the shift of a fluorescence spectrum was unobserved and fluorescence intensity was simply changed.

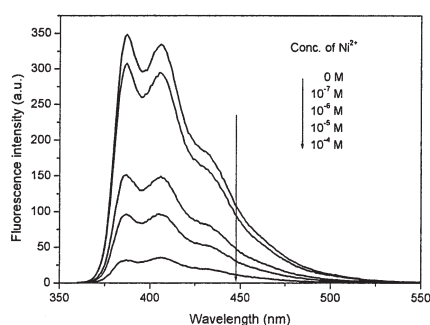


Figure 1. Fluorescence spectra changes of PFOxPy in DCE upon the addition of Ni²⁺.

As shown in Figure 2, most metal ion applicants except for Al³⁺ led to fluorescence quenching. The fluorescence quenching efficiency depended on the kind of the metal ion. Among the metal ion applicants, Ni²⁺ exhibited highest fluorescence quenching ability. This fluorescence quenching effect can be explained by the photoinduced electron transfer (PET) from the polymer to metal ions. On the contrary, Al³⁺ showed slight fluorescence enhancement. Consequently, all metal ions did not quench the fluorescence of PFOxPy and, as a result, the polymer exhibited selectivity to metal ions.

To investigate further the interaction between the polymer and metal ions, the ¹H NMR analysis was conducted. To a CDCl₃ solution of PFOxPy, one equivalent of NiCl₂·6H₂O in a small amount of CD₃OD was added. The aromatic peaks in the fluorene and pyridine group of this sample (δ = 8.58, 8.39, 8.31 and 8.07 ppm) shifted downfield relative to the metal ion-free sample, which revealed the coordination of a metal ion with 2,6-bis(1,3,4-oxadiazol-2-yl)pyridine even in the ground state.

In conclusion, the metal ion recognition property with a new conjugated polymer PFOxPy was evaluated. The selective interaction between metal ions and 2,6-bis(1,3,4-oxadiazol-2-yl)pyridine in the polymer backbone generally led to fluorescence quenching of the polymer through the PET process from the

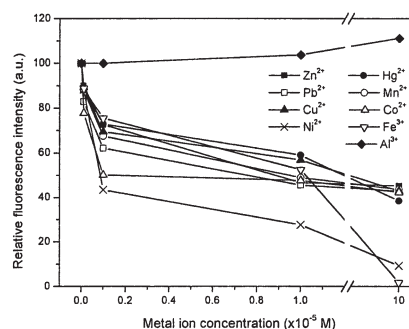


Figure 2. Dependence of fluorescence intensity of PFOxPy to the concentration of metal ions. The fluorescence intensity at 389 nm was monitored.

polymer to metal ions. This polymer showed the potential of these series of polyoxadiazoles with well-designed structures as competitive chemosensor materials due to the facile synthesis and low cost of chemicals for polyoxadiazoles.

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References and Notes

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- 11 Analytical datum of PePFOxPy: IR (KBr, cm⁻¹): 3274 (N-H), 2924, 2852, 1647 (C=O), 1490, 1460, 1295, 1236, 1122, 1074, 1001, 839, 748, 650.
- 12 Analytical data for PFOxPy: IR (KBr, cm⁻¹): 3076, 2923, 2852, 1541 (C=N), 1457, 1250, 1167, 1112, 1075, 964 (C-O-C), 899, 828, 778, 738; ¹H NMR (CDCl₃, ppm): δ = 8.56 (2H), 8.36 (4H), 8.22 (1H), 8.03 (3H), 2.26 (4H), 1.13 (36H), 0.80 (4H), 0.66 (6H); ¹³C NMR (CDCl₃, ppm): δ = 166.4, 163.2, 152.4, 144.4, 143.9, 138.7, 126.9, 125.3, 123.0, 121.9, 121.2, 56.2, 40.4, 31.8, 29.5 (br), 22.6, 14.0.