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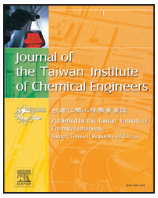

Synthesis and selective colorimetric detection of iodide ion by novel 1,5-naphthyridine-based conjugated polymers

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ABSTRACT

A highly selective colorematric detection of iodie ion based on 1,5-naphthyridine-based conjugated polymers (CPs) is reported. The synthesis of these new conjugated copolymers poly(2-(2-methoxyphenoxy)-6-(3-methoxyphenoxy)-1,5-naphthyridine)-p-bisdodecyloxyphenylene vinylenes) (**P1**) and poly(2-(2-methoxyphenoxy)-6-(3-methoxyphenoxy)-1,5-naphthyridine)-p-bis-2-(ethyl-hexyloxy)-phenylene vinylenes) (**P2**) was achieved by the Horner-Emmons polymerization reaction. These polymers were characterized by ^{1}H NMR, FT-IR and UV–vis spectroscopy and their bandgaps (**P1** = 2.35 eV; **P2** = 2.25 eV) were determined by cyclic voltammetric measurements. In colorimetric sensing, both these polymers can selectively detect iodide ion in a mixture of water and THF in the presence of a wide range of competing ions including F^-, Cl^-, Br^-, $NO_3{}^-$, CH_3COO^-, $SO_4{}^{-2}$, $SO_3{}^{-2}$, $S_2O_3{}^{-2}$ and CN^- and exhibit high sensitivity with LOD of 6.5 and 4.5 ppm, respectively. In the sensing protocol, the addition of aqueous solution of iodide salts to the colorless solution of polymers resulted in bare-eye color change from colorless to yellow, along with concomitant changes in the UV–vis spectra. The time dependent and concentration based studies revealed that **P2** was more sensitive and quick in response as compared to **P1**.

1. Introduction

Iodide anion (I^-) is among the most biologically essential ions since it plays an important role in controlling metabolic processes, cell growth of humans and animals [1] and sustaining neurological activity and thyroid gland function [2]. However, its imbalance in the body can cause serious risks to human health and may lead to numerous pathological ailments. For instance, deficiency of iodine results in the developmental delays, mental retardation and endemic goiter. Similarly, high iodine levels may lead to various ailments like hypothyroidism, hyperthyroidism, autoimmune thyroid and sometimes cancers [3,4]. In addition, elemental iodine is widespread in the environment due to its extensive use in the synthesis of medicines, organic dyes and chemicals [5]. Therefore, the development of a rapid, sensitive and selective detection of iodide ion in the food, pharmaceutical products and biological samples is of high importance.

Most of the currently available spectroscopic and electrochemical techniques for the detection of I^- suffer from limitations of requirement of long time for analysis and high volume of analyte [6]. On the other hand, low hydrogen bonding ability of I^-due to its large ionic radius and low charge density makes its sensing by chemosensors very difficult, in particular in aqueous solution [4]. Consequently, the design of chemosensors for the selective detection of iodide remains a formidable task [7]. The widespread applications of CPs in the development of optoelectronic devices have made them the subject of intense research [8,9]. By varying the donor and acceptor counterparts, the donor-acceptor methodology has allowed access to a wide range of conducting polymers with optical band gaps of the desired magnitude or frontier orbitals of the proper energies in device applications [10]. Moreover, the solubility of polymer in common organic solvents and its subsequent processability is also an important factor. Therefore, long flexible side chains to the backbone of the CPs are attached to make them more soluble in common solvents [11–14]. The high sensitivity of CPs is generally linked to “signal-amplification” or molecular wire effect, which arises due to the transfer of excitation energy along the whole backbone [7,13,14]. Moreover, anionic receptors affixed to the backbone or as pendant side-chains of CPs offer high selectivity in the detection of iodide ion [12,15].

In our ongoing effort towards the synthesis of CPs [13,16–19], we now wish to disclose the synthesis and colorimetric iodide ion sensing of two new CPs namely poly(2-(2-methoxyphenoxy)–6-(3-methoxyphenoxy)–1,5-naphthyridine)-p-bisdodecyl-oxyphenylene

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vinylene) (**P1**) and poly(2-(2-methoxyphenoxy)–6-(3-methoxyphenoxy)–1,5-naphthyridine)-p-bis-2-(ethyl-hexyloxy)-phenylene vinylenes) (**P2**). The design of these polymers is based on a central dialkoxyphenylene core (donor), paradisubstituted by two 2-methoxyphenoxy-6-(3-methoxyphenoxy)–1,5-naphthyridine through a vinylene linker (acceptor). We envisioned that the electron-deficient N-substituted 1,5-naphthyridine system may act as a π acid and facilitate recognition of iodide ion through anion-π interaction. Such non-covalent binding of electron deficient aromatic rings with anions has been widely known for its important role in several chemical and biological processes [20–22]. To our contentment, both **P1** and **P2** were able to sensitively and selectively detect iodide ion in the presence of a wide range of competing ions including F^-, Cl^-, Br^-, $NO_3{}^-$, CH_3COO^-, $SO_4{}^{-2}$, $SO_3{}^{-2}$, $S_2O_3{}^{-2}$ and CN^- as well as in the presence of various metal cations such as Li^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Cd^{2+} and Zn^{2+}.

2. Experimental

2.1. Materials and instruments

^{1}H and ^{13}C NMR were recorded on 500 MHz spectrometer (JEOL JNM-LA, JEOL USA Inc.) and Infrared spectra on FTIR spectrophotometer (Perkin Elmer 16F PC, Perkin Elmer Inc. USA). The Cary 5000 spectrophotometer (UV–vis-NIR, Agilent Technologies) was used for UV–vis absorption spectra and fluorescence emission spectra were recorded on FL3–2iHR (Horiba Jobin YVON) spectrofluorometer. The UV–vis and PL measurements of both polymers were performed using 2 mg/mL in THF. For Cyclic voltammetry (CV) measurement, scan rate of 100 mV/s was employed. Polymer film drop casted over gold disk electrode was used as a working electrode whereas Ag/AgCl/3 M KCl and a platinum sheet were used as reference electrode and auxiliary electrode, respectively. GPC analysis were performed on Agilent PL-GPC 220 High Temperature GPC/SEC System, using polystyrene standards as referenec and THF as an eluent. Thermogravimetric analysis (TGA) was measured on SDT Q600 (V20.9 Build 20) thermal analyzer. Within the oxygen atmosphere, samples were heated from room temperature to 800 °C at a rate of 10 °C/min rise, employing purge rate of 50 mL/min.

2.2. Synthesis of 4,4′-((1,5-naphthyridine-2,6-diyl)bis(oxy))bis(3-methoxybenzaldehyde) (**6**)

Under the positive pressure of nitrogen, an oven-dried round bottom flask was charged with a magnetic stir bar, copper (I) iodide (0.13 g, 0.69 mmol), picolinic acid (0.17 g, 1.39 mmol), **4** (2.54 g, 16.68 mmol), **5** (2.0 g, 6.95 mmol) and K_3PO_4 (4.81 g, 27.8 mmol) followed by the addition of dimethylsulfoxide (10 mL) via syringe. The mixture was heated at 80 °C for 24 hr until completion of reaction (TLC analysis). After cooling to room temperature, ethyl acetate (20 mL) was added and the organic layer was washed with sat. $NaHCO_3$ (5 mL x 2). After separation of organic layer, the aqueous layer was re-extracted with ethyl acetate (10 mL x 2). The combined organic layer was washed with sat. NaCl (5 mL), dried with Na_2SO_4 and then passed through a pad of silica gel. The filtrate was concentrated under reduced pressure and the obtained residue was resolved over silica column, eluting with ethyl acetate: hexanes (1:4) to afford compound **6** as pale yellow solid (Yeild, 86%; M.P., 134–135 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.00 (s, 2H), 8.31 (d, 2H, J = 9.15 Hz), 7.83 (d, 2H, J = 8.8 Hz), 7.63 (d, 2H, J = 8.8 Hz), 7.57 (d, 2H, J = 6.9 Hz), 7.41 (b, 2H, J = 4.9 Hz), 7.39 (d, 2H, J = 4.9 Hz), 3.80 (s, 6H). ^{13}C NMR (125.6 MHz, $CDCl_3$): δ 191.11, 161.25, 152.45, 147.36, 140.12, 137.96, 134.75, 129.32, 125.13, 123.54, 116.70, 111.15, 56.07. FT-IR (KBr): 3070, 2923, 2833, 2743, 1690, 1581, 1477, 1386, 1278, 818 cm^{-1}. Anal. Calcd for $C_{24}H_{18}N_2O_6$: C, 66.97; H, 4.22; N, 6.51. Found: C, 66.91; H, 4.27; N, 6.44.

2.3. Synthesis of ***p1***

Under nitrogen atmosphere, sodium tert–butoxide (0.17 g, 1.74 mmol) was added to a solution of dialdehyde **6** (0.15 g, 0.35 mmol) and monomers **2** (0.26 g, 0.35 mmol) in anhydrous DMF (20 mL) and mixture was then heated at 100 °C for 24 h. The reaction was cooled to room temperature, poured into 75 mL of methanol and centrifuged to get the product after decantation of the solvent. To remove small molecule impurities and oligomers, the residue was re-dissolved in THF and re-precipitated successively from methanol, isopropanol, and hexane to afford **P1** as a dark yellow solid (80%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (br., 2H), 7.47 (br., 2H), 7.44 (br., 2H), 7.20 (br., 2H), 7.15 (br., 2H), 7.11 (br., 2H), 7.09 (br., 2H), 7.05 (br., 2H), 4.07 (br., 4H), 3.81 (br., 6H), 1.90–1.85 (br., 4H), 1.53 (m, 4 H), 1.33 (m, 32H), 0.85 (br., 6H). FT-IR (KBr): 3025, 2925, 2849, 1596, 1502, 1356, 1245, 1029, 825 cm^{-1}. GPC analysis: $M_n = 3340$, $M_w = 5720$, PDI = 1.70. Anal. Calcd for $(C_{56}H_{72}N_2O_6)_n$: C, 77.38; H, 8.35; N, 3.22. Found: C, 76.86; H, 8.58; N, 2.90.

2.4. Synthesis of ***p2***

The reaction of dialdehyde **6** and monomer **3**, as per procedure described for the synthesis of **P1**, gave **P2** as a light yellow solid (55%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (br., 2H), 8.02 (br., 2H), 7.84 (br., 2H), 7.61 (br., 2H), 7.45 (br., 2H), 7.35 (br., 2H), 7.19 (br., 2H), 7.15 (br., 2H), 3.96 (br., 4H), 3.79 (br., 6H), 2.06 (br., 4H), 1.92–1.85 (br., 4H), 1.53 (m, 4H), 1.32 (m, 20H), 1.01 (br., 6H), 0.91 (br., 6H). FTIR IR (KBr): 3076, 2923, 2854, 1593, 1507, 1473, 1349, 1278, 1031, 830 cm^{-1}. GPC analysis: $M_n = 3618$, $M_w = 5930$, PDI = 1.62. Anal. Calcd for $(C_{48}H_{58}N_2O_6)_n$: C, 76.16; H, 7.46; N, 3.70. Found: C, 75.84; H, 7.68; N, 3.38.

2.5. Sensing of iodide ions

For iodide sensing, solutions of polymers in THF (0.0144 mM) and salts in water (125 ppm) were prepared. Both polymers exhibited yellow colour in THF solution at higher concentrations or in the solid state whereas they become colourless to bare-eye at lower concentration (0.0144 mM). This concentration was chosen for iodide ion sensing analysis. The colorimetric detection limit was monitored for varied concentrations and time dependent analysis by UV–vis (Jasco v-670, spectrophotometer, Japan) measurements.

3. Results and discussion

3.1. Synthesis and characterization

The synthesis of polymers **P1** and **P2** required the synthesis of monomers **2** and **3**, which in turn were synthesized by employing literature known procedures (Scheme 1) [13]. Likewise, synthesis of monomer dialdehyde **6** was realized by the Ullman's reaction between vanillin (**4**) and 2,6-dibromo-1,5-naphthyridine (**5**) in DMSO at 80 °C, using picolinic acid and copper(I) iodide as catalysts. The purifications of the desired **6** required passing the crude product through a pad of silica first, in order to remove colored impurities, followed by purifications with column chromatography to afford the desired dialdehyde **6** in 86% yield. Next, Horner-Emmons reaction of dialdehyde **6** with monomers **2** or **3** in DMF under heating

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