



Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Facile preparation and fluorescence properties of a soluble oligopyrrole derivative



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ARTICLE INFO

Article history:

Received 29 January 2015

Received in revised form 20 April 2015

Accepted 25 April 2015

Available online 29 April 2015

Keywords:

Synthesis

Soluble

Oligopyrrole derivative

Fluorescence

ABSTRACT

A soluble oligopyrrole derivative (OMDPP) was prepared based on a bipyrrrole monomer 2-methyl-1,3-di(1H-pyrrol-1-yl) propan-1-one (MDPP) using chemical oxidation method. The characterization of the chemical structure indicated that OMDPP was mainly generated from the coupling of the pyrrole ring attached to the methylene group in the monomer. Our results also proved that OMDPP exhibited good solubility and film-forming ability. The fluorescence properties of OMDPP solutions were then characterized, and green emissions were observed in the wavelength range of 550–564 nm in a variety of solvents under the excitation wavelength of 467 nm. The research of solvatochromic behavior of OMDPP revealed that the electron donating-accepting property of the solvent possibly have greater impact on the Stokes shift of OMDPP solution compared with the polarity of the solvent. Additionally, the concentration (from 5*E-6 g/ml to 8*E-4 g/ml) and the excitation wavelength (287–507 nm) also exhibited obvious influences on the emission spectra of the OMDPP solution, which were investigated in detail.

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1. Introduction

Conjugated organic oligomers have attracted much attention during the past few years due to their good solubility, excellent electronic and photophysical properties, as well as superior film-forming and self-assembling abilities [1,2]. Based on those attractive features, conjugated oligomers are regarded as one of promising materials for fabricating electronic and optoelectronic devices [3,4].

Among a large number of conjugated oligomers, pyrrole oligomers and their derivatives are one of the most studied topics because of their unique molecular structures and wide distribution in natural products. For instance, the pyrrole oligomer species can act as complexants for cations due to the electron-donating ability of N atom in the pyrrole ring [5]. Meanwhile, pyrrole oligomer species are capable of binding anions and neutral substrates through hydrogen bonding, which could occur at the pyrrolic N–H moiety [6]. In addition, the intermolecular π – π stacking makes it

feasible for pyrrole oligomers to form supramolecular assemblies under suitable conditions [7].

Numerous methods have been developed for the synthesis of oligopyrroles with various structures, such as Vilsmeier condensation, Paal–Knorr cyclization, dipolar cycloaddition, Ullmann coupling and other metal-mediated coupling reactions [8–11]. Generally, these methods involve drastic reaction conditions and tedious procedures more or less. It is well known that ferric chloride can be used as an oxidant for the polymerization of pyrrole to form insoluble and infusible polypyrrole with simple and mild reaction conditions. However, this method has rarely been applied to induce the oxidative coupling of monomers to prepare soluble oligopyrroles.

In this study, the simple preparation of a soluble oligopyrrole derivative (OMDPP) is reported. The oligomer OMDPP was synthesized based on the dipyrrole monomer MDPP through the direct induction with ferric chloride as the oxidant. The molecular structure and formation mechanism of OMDPP were discussed. In addition, the optical properties of OMDPP solutions were characterized by UV–vis absorption and fluorescence spectroscopy. The effects of the solvent, oligomer concentration and the excitation wavelength on the fluorescence properties of OMDPP solution were also investigated in detail.

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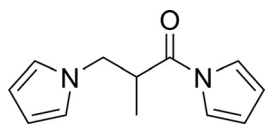


Fig. 1. The chemical structure of MDPP.

2. Experimental

2.1. Materials

Iron (III) chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, analytical grade) and analytical grade solvents of tetrahydrofuran (THF), dichloromethane (DCM), *N*-methylpyrrolidone (NMP), dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were purchased from Sinopharm Chemical Reagent Co. Ltd. and used without further purification. The monomer of MDPP as shown in Fig. 1 was synthesized according to the procedures reported elsewhere [12].

2.2. Preparation of OMDPP

MDPP (0.606 g) was added to 80 ml deionized water with stirring in the reaction vessel and then 20 ml pre-prepared solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.375 M) was added dropwise. The mixture was then allowed to react for 36 h at 18–20 °C. When the reaction was terminated, the solvent was poured out and the black sticky residue was collected. The product was washed with deionized water several times until the filtrate was colorless. After vacuum drying at 40 °C for 24 h, the oligomer OMDPP was obtained. Yield = 65%; Molecular weight: $M_n = 583$ and $M_w = 633$; ^1H NMR (DMSO- d_6 , 400 MHz), δ (peak, area integral): 7.47 (s, 1.90), 6.75 (s, 1.17), 6.31 (s, 2.06), 5.94 (s, 1.59), 4.26 (m, 1), 4.02 (m, 0.93), 3.85 (m, 1.02), 1.14 (d, 3.06); ^{13}C NMR (DMSO- d_6 , 100 MHz), δ : 172.97, 122.98, 121.40, 119.70, 118.88, 113.56, 109.365, 108.02, 107.69, 98.12, 55.00, 51.28, 43.91, 42.18, 37.92, 31.41, 22.80, 20.57, 16.19; Elemental analysis: calculated for $\text{C}_{36}\text{H}_{38}\text{N}_6\text{O}_3$: C, 71.29%, H, 6.31%, N, 13.95%, O, 7.97%. Found: C, 68.86%, H, 6.281%, N, 12.14%, O, 8.679%; Decomposition temperature: 127 °C (TG analysis); FTIR (KBr, cm^{-1}): 3146, 3105 and 732 cm^{-1} (pyrrole ring C—H), 2980, 2938 and 1371 cm^{-1} (saturated C—H), 1710 cm^{-1} (C=O), 1547, 1467 and 1285 cm^{-1} (pyrrole ring stretching vibration).

2.3. Characterization

The chemical structure of the product was identified by Fourier transform infrared (FTIR) spectroscopy (Nicollet AVATAR-IR

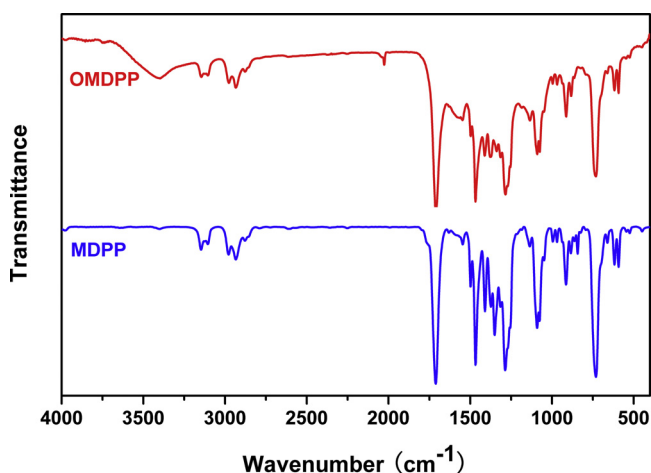


Fig. 2. IR spectra of OMDPP and MDPP.

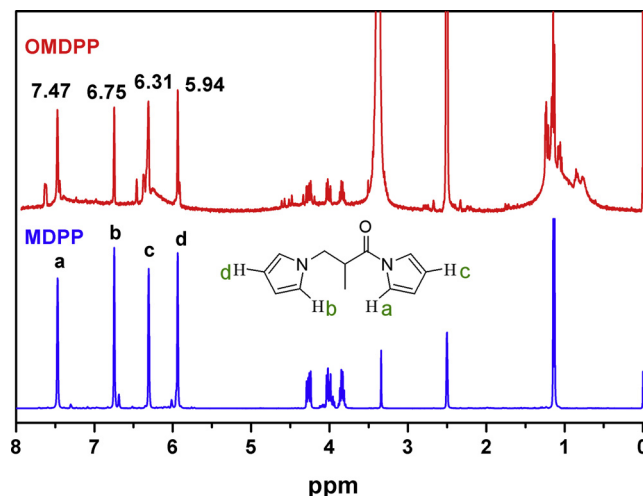


Fig. 3. ^1H NMR spectra of OMDPP and MDPP.

360 spectrometer) and NMR spectroscopy (Bruker Advance 400 MHz spectrometer). Gel permeation chromatography (GPC) measurement was carried out in THF with a Waters-Breeze instrument to determine the molecular weight of the product. The thermal stability of OMDPP was tested using a Netzsh TG209C analyzer under a nitrogen atmosphere. The morphology of the cast film of OMDPP was observed using scanning electron microscope (SEM-VE9800S). The organic composition (C, H, N and O) of OMDPP was measured by elemental analyzer (Vario EL, Elementar Analysensysteme GmbH). The fluorescent image was captured using Nikon Eclipse 80i microscope. UV–vis absorption spectra were recorded on a UV-2550 spectrophotometer in quartz cuvettes. Fluorescence was measured with solutions in an F900 fluorescence spectrometer (Edinburgh Instruments).

3. Results and discussion

3.1. Structure characterization of OMDPP

The FTIR spectrum of OMDPP is shown in Fig. 2. The peaks at 1547 cm^{-1} and 1467 cm^{-1} are the characteristic absorptions of pyrrole ring corresponding to the antisymmetric and symmetric C=C stretching vibration [13]. The peak at 1710 cm^{-1} corresponds to C=O stretching vibration. The saturated C—H bonds exhibit the absorptions at 2980, 2938 and 1371 cm^{-1} , respectively. Additionally, it is observed that the FTIR spectrum of OMDPP displays small changes compared with that of the monomer MDPP. The peak at 732 cm^{-1} , corresponding to the C—H bonds from the pyrrole ring [14], seems slightly weaker. It indicates that the pyrrole ring of the monomer coupled partially.

In order to identify the structure of OMDPP, the ^1H NMR spectrum was recorded by dissolving the sample in deuterated dimethyl sulfoxide (DMSO- d_6). The coupling positions of the integral area of the proton signals originating from pyrrole rings (the chemical shifts of 7.47, 6.75, 6.31 and 5.94 ppm), as shown in Fig. 3. In the ^1H NMR spectrum of the monomer, the integral areas of chemical shifts of 7.47, 6.75, 6.31 and 5.94 ppm were 1.99, 2.06, 2.02 and 2.07, whereas the integral areas of oligomer's spectrum became 1.90, 1.17, 2.06 and 1.59, correspondingly, with maintaining the integral area of proton from methylene group (the chemical shifts of 4.26 or 4.02 ppm) as 1. The results indicate that the oligomer OMDPP was mainly generated from the coupling of the pyrrole ring connected with the methylene group. A few pyrrole rings connected with the carbonyl group also took part in the

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