



Photo switchable pendant furyl and thienyl fulgimides containing polypyrroles



Sivasankaran Nithyanandan, Palaninathan Kannan*

Department of Chemistry, Anna University, Chennai 600 025, India

ARTICLE INFO

Article history:

Received 16 May 2013

Received in revised form

26 July 2013

Accepted 19 August 2013

Available online 28 August 2013

Keywords:

Electropolymerization

Photochromism

Furyl fulgimide

Thienyl fulgimide

Polypyrrole

ABSTRACT

We report the new pendant furyl and thienyl fulgimides photochromic switch bearing polypyrroles. The functionalized pyrrole monomers synthesized and structures are ascertained by NMR and mass spectral techniques. The yield of fulgides and fulgimides are improved by using trifluoroacetic anhydride (TFA) as a dehydrating agent. The photo-switching properties of fulgimides monomers are explained by electronic structures of HOMO–LUMO of the monomers using Gaussian 03 packages. The electro-active polymer films deposited on indium tin oxide (ITO) electrodes are characterized by cyclic voltammetry and atomic force microscopy (AFM). The electrochemically formed thin films undergoes photo-switching between open and closed state of fulgimides moiety. The photo-switching properties of the polymer films have been confirmed by UV/vis spectroscopy. Though the films are photochemically stable, their mechanical stability with respect to adhesion to electrode is found to be sensitive to the solvent and electrode material.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Photochromic materials are playing a vital role in photo-switching devices [1–6]. On the basis of reversible change in molecular and electronic structures of photo-responsive compounds upon illumination many physical properties can be switched. The design of a switch using molecules that have bi-stable states is of particular interest in molecular electronics. Molecular electronics can be defined as the study of electrical and electronic processes by accessing the individual molecules with electrodes and exploiting molecular structure to control flow of electrical signals through them. There is an intense interest in fabricating materials with photonic band-gaps in visible, infrared, and microwave spectral regions. The idea is to develop photochromic materials used as light waveguides, where light is set them apart from non-molecular semiconducting and conducting materials used for processing information [7–10]. Although the syntheses of polymeric materials from pyrrole derivatives were well known [11–14], the intensive research efforts have been focused on optimization of preparation methods [15]. Polypyrrole is prepared by two routes, namely, chemical or electrochemical polymerization methods [16]. However, it is evident for the polymers produced by chemical synthesis

contain a significant proportion of regiochemical defects. Electrochemistry has played a key role in the synthesis and characterization of novel polymeric materials. Electrochemical techniques are particularly suitable for controlled synthesis of these functionalized electroactive polymers and for tuning of a well-defined oxidation state. The preparation, characterization and application of electrochemically active and electronically conducting polymeric systems are still in the foreground of research activity in electrochemistry. Electropolymerization of heteroaromatic monomers to form π -conjugated polymers has been well-documented [11]. The electropolymerizable monomers such as thiophene, aniline, pyrrole, and carbazole are of interest, as it can yield unique polymerization mechanism and electro-optical applications. The mechanism goes through a radical cation coupling accessed through potentiodynamic or potentiostatic methods [13,14].

Furthermore, electrochemical polymerization of monomer is the most convenient, simple and robust method to prepare polymer films [16]. *In situ* formation of polymers on electrode materials by electrochemical techniques [17] is a well-established approach and focused primarily on fabrication of conducting polymer films [18], providing electroactive polymer film layers, for example, retaining biomolecules on surfaces [19,20]. In addition, functionality of both monomers and polymers can be extended by introducing responsive units that can be switched between two states using external stimuli, e.g., light, heat or redox switching. For instance, the introduction of photo controlled switching units into

* Corresponding author. Fax: +91 44 22200889.

E-mail address: pakannan@annauniv.edu (P. Kannan).

a monomer to control its electropolymerizability could offer considerable opportunities in device fabrication. Periodically, dithienylethene switches have been explored to be a good platform to build functional molecular-based systems, allowing reversible control of properties. Even though several studies on gold nanoparticles capped with other photochromic molecules were reported [21,22], excited-state of organic molecules on noble metal surfaces is readily quenched by surface plasmon resonance [23]. Therefore, it is essential to develop technology to avoid surface plasmon quenching. The present work deals with synthesis of heterocyclic furyl and thienyl fulgimides functionalized pyrrole monomers and then electropolymerized as thin films on ITO substrate [24]. The photo physical and electrochemical properties of synthesized polypyrroles have been compared and discussed.

2. Experimental

Chemicals and solvents were purchased from Aldrich, Acros or Merck. All solvents used in the reactions were distilled freshly from appropriate drying agents before use. The synthetic procedure of intermediates 3-furyl fulgide, furyl diacid, monoamide and 3-thienyl fulgide was earlier reported with little modification [25]. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-400 spectrometer. Chemical shifts (δ) were reported in parts per million relative to internal standard tetramethylsilane (TMS). Mass spectra (MS) were recorded using an LCQ Advantage mass spectrometer. High-resolution mass spectra (HRMS) were recorded on a VG ZAB-MS mass spectrometer. Thermogravimetric analysis (TGA) measurement was performed with a TA instrument SDT-TG Q600 under N_2 atmosphere, at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. UV spectra were recorded on a Shimadzu UV1650PC spectrophotometer. Cyclic voltammetry (CV) measurements were performed on a CHI 600D electrochemical analyser at room temperature with three-electrode cell in a solution of Bu_4NClO_4 (0.1 M) in dichloromethane at a scanning rate of 100 mV s^{-1} . A platinum foil was used as a counter electrode, ITO/glass substrate was used as a working electrode and an Ag/AgCl electrode as a reference electrode. After measurement the reference electrode was calibrated with ferrocene (Fc). ITO conductive glass electrodes (Sigma Aldrich) were used to obtain the UV–visible spectra of the electropolymerized films. Illumination experiments of the electrodeposited films were performed using an Oriel Instrument 30 W mercury lamp.

2.1. Theoretical calculations

Density functional theory has a good track record in terms of predicting the electronic structure of fulgimide molecules [13]. DFT has been used to determine the ground state properties (i.e., optimized geometries, vibrational spectra, and so on). Most of the calculations were performed with Gaussian 03 suite of programs [16]. No constraints were imposed during geometry optimizations.

2.2. Synthesis of furyl fulgide (FF)

The furyl diacid (FDA) (2 g, 7.19 mmol) was dissolved in dichloromethane (40 ml) to give a dark orange-red solution which was cooled in an ice–salt–water slush. Upon addition of trifluoroacetic anhydride (2 ml) dissolved in dichloromethane (20 ml), the solution turned into deep purple. After being stirred at room temperature for 3 h, the mixture was poured onto ice–water slush. The product was extracted with ether until the extracts were colourless, and the combined organic phases were washed with 10% aqueous sodium hydrogen carbonate. The ether solution was dried (Na_2SO_4) and evaporated to dryness under reduced pressure to give a red oil, which afforded furyl fulgide as yellow crystals. ^1H

and ^{13}C NMR values are matched with reported literature [26]. Similarly, the same procedure was adopted for synthesis of thienyl fulgide (TF).

2.3. Synthesis of furyl fulgimide (FM)

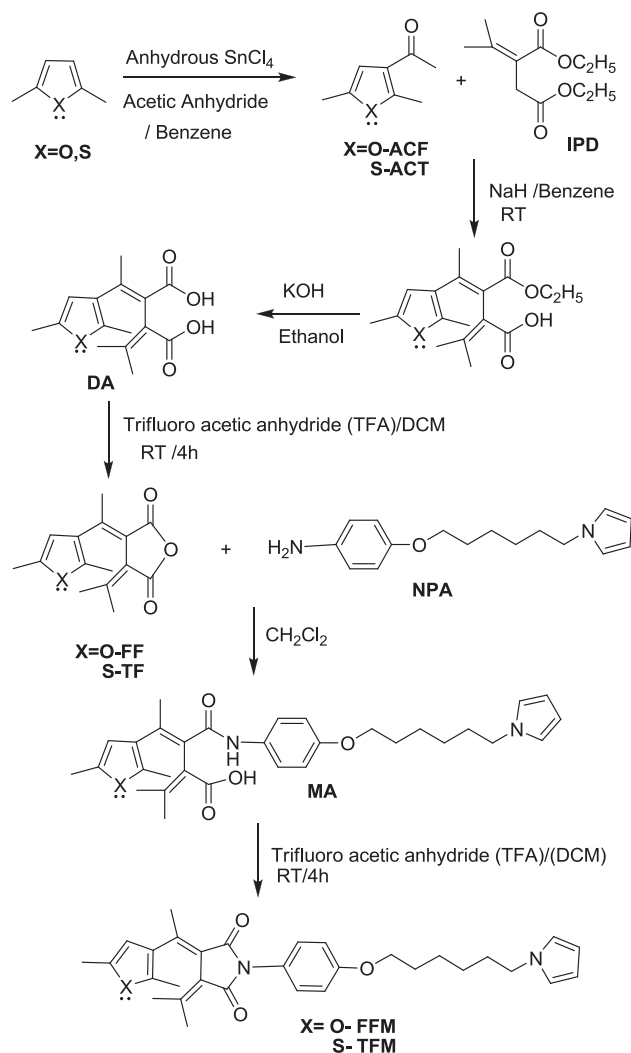
2.3.1. Step a)

The furyl fulgide (0.7 g, 2.54 mmol) and 4-(N-hexyl pyrrole) aniline (0.66 g, 2.53 mmol) were dissolved in 50 ml of dichloromethane, and treated at $40\text{ }^\circ\text{C}$ for 3 h. The solvent was then evaporated, and crude product was purified by column chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 9:1) to yield 1.22 g (89%) of monoamidated (MA) product.

^1H NMR (400 MHz, CDCl_3 , δ in ppm): 1.8 (s, 3 H), 1.9 (s, 3H), 2.1 (s, 3H), 2.2 (s, 3H), 2.3 (s, 3H), 4.3 (s, 2H), 5.8 (s, 1H), 6.4 (s, 1H), 7.1 (d, $J = 8.1\text{ Hz}$, 2H), 7.3 (m, 1H), 7.5 (dd, $J = 3.5\text{ Hz}$, 1H), 7.7 (d, $J = 7.6\text{ Hz}$, 2H), 7.8 (m, 1H), 8.4 (d, $J = 8.1\text{ Hz}$, 1H), 8.6 (s, 1H), 8.7 (m, 2H). ^{13}C NMR (400 MHz, CDCl_3 , δ in ppm): 13.3, 15.1, 21.8, 30.9, 44.0, 118.8, 121.3, 121.5, 123.9, 124.4, 126.2, 127.5, 128.5, 133.1, 136.6, 137.0, 137.5, 137.9, 138.3, 148.6, 149.2, 149.7, 156.0, 156.7, 171.4.

2.3.2. Step b)

The monoamide (MA) (1.18 g, 2.19 mmol) was then treated by trifluoroacetic anhydride (2 ml dissolved in 5 ml of CH_2Cl_2) at room



Scheme 1. Synthesis of monomers FFM and TFM.

Download English Version:

<https://daneshyari.com/en/article/5202263>

Download Persian Version:

<https://daneshyari.com/article/5202263>

[Daneshyari.com](https://daneshyari.com)