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Photochromic switchable pendant indolyl fulgimide polypyrrole

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ABSTRACT

The photochromic switchable 2-indolyl fulgimide functionalized pyrrole monomer is synthesized and ascertained by spectroscopic techniques. The absorption and emission band of monomer due to intramolecular charge transfer (ICT) state exhibit typical bathochromic shift from nonpolar to polar solvents. The molecular geometry and bandgap energy of monomer in open form as well as closed form are calculated by B3LYP/6-31 G (d) with Gaussian 03 program package. The functionalized pyrrole monomer is electropolymerized by cyclicvoltammetric method on an electrode. The polymer indicated a completely reversible photoswitching between two isomers of open and closed form 2-indolyl fulgimide moiety, which are stable over many cycles of operation by UV/visible light sources. The closed form of polymer exhibit fluorescence quenching attributed to the energy transfer from conductance band of polypyrrole to closed form of 2-indolyl fulgimides unit. This fluorescence quenching system controls the conductance of conducting polymer in molecular electronics and molecular switches.

1. Introduction

Organic photochromic materials are considered to be viable materials for storage of information because of their reversibility. It has significance in the area of ‘smart’ materials, and potential use as components in molecular electronics, optical memory, and variable-transmission filters [1–6]. In addition, photochromic materials also act as molecular switches that will turn the electrical appliances “on” and “off”, and also store the information at the molecular level. These materials can act as potential candidate to influence the development of optoelectronic materials and information technologies [7]. Usually, molecular switches act as switching unit in various optoelectronic devices and functional materials upon photo-illumination. Alternatively, a photo-switch exhibits two stable and selectively addressable states. This photoinduced changes in chemical and physical properties of photochromic molecule is of great interest, because of its potential applications for ultra-high density optical data storage and photo-regulated molecular switches [8]. Two isomers of photochromic molecule communicate with other chromophores make a possible construction of all photonic Boolean logic gates [9]. Currently the photochromic molecules are explored in photonic amplifiers, data and signal processing [10]. The inputs of such systems are constituted by photonic stimuli that initiate photochromic cyclization process; meanwhile the output reading typically relies on variations of absorption and fluorescence measurements. Prominent characteristics of photochromic materials are their reversible switching paired with often high fatigue resistance.

Conductance of photoswitching in the photochromic diarylethene and dithienylethene on gold and silver nanoparticles respectively, are well reported [11,12]. In these photoswitching process of the diarylethene and dithienylethene was completely non-reversible due to the SPR phenomena. From this result indicates that the loss of photochromic reversibility of diarylethene [13]. To overcome this drawback of surface plasmon resonance in photochromic material such as diarylethene and fulgimide can be functionalized on polypyrrole conducting polymers. To best of our knowledge, there is no such work was reported so far. Here we report Indolyl fulgimide [14,15], which is considered as the most promising photochromic compound. It undergoes back-and-forth photoisomerization, whose colour can be reversibly changed upon illuminating with ultraviolet and visible light. Further, the fulgimide is never ever bleached at room temperature. Thus, the photochromic medium can be written and erased by specified wavelength of particular interest. This article mainly focused on synthesis of polypyrrole bearing photo-switchable fulgimide moiety via electropolymerization on ITO substrate. Further the gowned ITO substrate is investigated in detailed manner.

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2. Experimental

2.1. Materials and measurements

Pyrrole and tetrabutylammonium perchlorate TBAP) were purchased from Sigma Aldrich and purified before use. The synthesis of 2-indolyl fulgide and N-bromohexyl pyrrole have been described and reported previously [16]. Electrochemical experiments were carried out with a conventional three electrodes cell and Electrochemical Analyzer/Workstation Model 600D. ITO conductive glass plates (area = 2×1 cm^2) were used as working electrode, a platinum wire as counter-electrode and an AgCl coated silver wire as a reference electrode. The ferrocinium/ferrocene redox potential was measured to 0.54 V versus the reference electrode, in acetonitrile 0.1 M Bu_4NClO_4. Electrolytic solutions were routinely deoxygenated with argon. ITO conductive glass electrodes (Sigma Aldrich) were used to obtain the UV–visible transmission spectra of the electropolymerized films. The working electrode was an ITO conductive glass with 0.8 cm (width) and 2 cm (length) dimension was flattened against the walls of cuvette orthogonal to light beam pathway. Platinum wire was used as counter electrode and AgCl coated Ag wire as reference electrode. ^1H and ^{13}C NMR spectra were recorded on a JEOL A-400 spectrometer. Mass spectra were taken with a JEOL JMS-700T mass spectrometer. UV–visible data were recorded by using a UV1650PC spectrophotometer. Fluorescence spectra were recorded by using Perkin Elmer LS-55 Fluorescence spectrometer. Thermogravimetric analyses were performed on a Mettler TC 10A at a heating rate of 10 °C/min under nitrogen atmosphere. Photoillumination was conducted using 150 W Mercury-xenon lamp (HEBER MICRO PHOTO REACTOR) as a light source. A photocyclization conversion of 2-indolyl fulgimide chromophores and switching studies were determined by UV–visible spectroscopy. AFM experiments were performed using an Agilent 5500 SPM system under ambient conditions. Height, amplitude, and phase images were simultaneously recorded in acoustic alternating current (AAC) mode with a typical scan rate of 1 Hz. Commercial silicon cantilevers (Nano World PPP-NCH) with a spring constant of 33–38 Nm^{-1} and resonance frequency of 280–320 kHz were used. Set-point amplitude was typically 75% of the free-oscillating amplitude. The morphologies of photochromic functionalized polypyrrole were examined using a JEOL JSM-5600 LV scanning electron microscope. The energy bandgap (E_g) of polymer was estimated from absorption wavelength. Computational details with geometry optimization of open form and closed form of monomer was performed with Gaussian 03 program at the hybrid DFT/B3LYP level of theory with the 6-31G (d,p) basis set [17]. The HOMO-LUMO gap is an important characteristic of the system that determines bandgap of open and closed form of fulgimide moiety.

2.1.1. Fluorescence lifetime measurements

Time-resolved fluorescence measurements were carried out using (IBH) time-correlated single photon counting techniques by exciting the sample at 375 and 550 nm. Fluorescence decay was measured at 470 and 550 nm. The data analysis was carried out by the software provided by IBH (DAS-6), which is based on deconvolution techniques using nonlinear least square method, and quality of the fit is normally identified by the value $\chi^2 < 1.2$ and weighted residual.

2.2. Electropolymerization

Electropolymerization process was carried out in 0.1 M Bu_4NClO_4/CH_3CN solutions containing 0.01 M 2-indolyl fulgimide functionalized pyrrole monomer. The film obtained by electropolymerization with sweep rate of 50 mV/s, potential range of 0 V–1.2 V with 30 cycles. The film washed thoroughly with acetonitrile to remove the unreacted monomer and excess of electrolyte. The counter ion of the perchlorate maintains the charge neutrality throughout the polymerisation. The quantity of electrodeposition was measured in thin film (mol/cm^2) by integration of the charge under the cyclicvoltammetric waves in deaereated 0.1 M Bu_4NClO_4/CH_3CN solution.

2.3. Synthesis of N-(4-(6-(1H-pyrrol-1-yl) hexyloxy) phenyl) aceta mide (2)

A mixture of N-(4-hydroxyphenyl) acetamide (1.31 g, 8.69 mmol) and N-(6-bromohexyl pyrrole (2 g, 8.69 mmol) were charged to 100 mL of acetone followed by potassium carbonate (4.7 g 34.7 mmol) and a catalytic amount of KI. The solution was then refluxed for 2 days. The reaction mixture was cooled to room temperature, the residual solid was filtered out and solvent from the filtrate distilled under reduced pressure. Thus obtained crude products were dissolved in 100 mL of dichloromethane. The organic layers were washed successively with aqueous hydrochloride (1 M), and then dried over sodium sulphate. The solvent was distilled under reduced pressure. The product was recrystallized from chloroform-hexane mixture to give 2 as a solid (2.5 g, 82% yield).

^1H NMR ($CDCl_3$, 400 MHz) δ: 7.52 (s, 1H), 7.37(d, 2H), 6.82 (d, 2H), 6.65 (d, 2H), 6.13 (d, 2H), 3.89 (t, 4H), 2.11 (s, 3H), 1.78 (m, 4H), 1.43 (m, 2H), 1.36 (m, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz) δ: 162.5, 147.5, 132.5, 130.2, 127.0, 126.1, 110.1, 41.8, 33.8, 32.6, 29.4, 27.7, 26.0. Anal. calcd for $C_{18}H_{24}N_2O_2$: C, 46.66; H, 4.18; N, 3.63. Found: C, 46.60; H, 4.23; N, 3.62%.

2.4. Synthesis of 4-(6-(1H-pyrrol-1-yl) hexyloxy) aniline (3)

2 g (7.75 mmol) of 2 was dissolved into 20 ml of ethanol and refluxed at 80 °C then sodium hydroxide (1 g) was added. The reaction mixture was maintained for 4 h. After cooling to room temperature, the solution was concentrated and quenched with chilled water. The product was extracted using 50 ml of diethyl ether and then dried over sodium sulphate. The solvent was evaporated. The product was recrystallized from ethanol to afford 3 as pale brown solid (1.45 g, 78% yield).

^1H NMR ($CDCl_3$, 400 MHz) δ: 6.97 (d, 2H), 6.73 (d, 4H), 6.23 (d, 2H), 3.9 (t, 4H), 3.41 (br, 2H) 1.78 (m, 4H), 1.43 (m, 2H), 1.36 (m, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz) δ: 162.5, 147.5, 132.5, 130.2, 127.0, 126.1, 110.1, 41.8, 33.8, 32.6, 29.4, 27.7, 26.0. Anal. calcd for $C_{16}H_{22}N_{2O}$: C, 74.38; H, 8.58; N, 10.84. Found: C, 75.0; H, 7.94; N, 10.45%.

2.5. Synthesis of 2-indolyl functionalized pyrrole monomer (4)

To round bottom flask is charged with a solution of 2-indolyl fulgide (0.301 g, 1 mmol) in benzene (15 mL), through a dropping funnel, 4-(6-(1H-pyrrol-1-yl) hexyloxy) aniline (90%, 0.2 g, 1 mmol) was diluted in benzene (5 mL) was added drop wise. The reaction mixture was allowed stirr for 1 h at room temperature. To this reaction mixture, zinc chloride powder (0.14 g, 1 mmol) was added in one portion. Subsequently, the reaction mixture was heated to reflux temperature (80 °C), followed by addition of hexamethyldisilazane (HMDS) (0.25 g, 1.5 mmol) in benzene (5 mL) through addition funnel, over a period of 5 min. This reaction mixture was further refluxed for 20 h. The benzene solvent was distilled by rotary evaporator. The crude product obtained was purified by means of flash silica gel chromatography column (chloroform as eluent) to afford a brown solid monomer (0.188 g, 47% yield).