



One-step synthesis of a new photoelectron-accepting, n-dopable oligo (pyrazole)



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ABSTRACT

A new photoelectron-accepting, n-dopable organic oligomer has been synthesized in a single step. It is a fluorescent tetramer formed from a substituted aminopyrazole, 3-amino-1H-pyrazole-4-carbonitrile, which has a low cost (about two USD per gram). Its chemical structure was verified using FTIR, mass spectrometry, and ¹H/¹³C NMR. When used as an electron acceptor in an ITO-supported photocell containing a PEDOT-PSS hole transporting layer, the tetramer can support photocurrents of as high as 1.40×10^{-4} A at 0 V bias, and 7.20×10^{-3} A above baseline at 1.0 V bias. The cell, having a fabrication method that is not yet optimized, showed a photodiode responsivity of as high as 0.48 A/W, and a sensitivity of as high as 6.0×10^{-4} Sm/W. Most importantly, it also demonstrated a detectivity of as high as 2.7×10^{12} Jones, which is comparable to state-of-the-art inorganic photodiodes. The tetramer may represent a new, very inexpensive class of conducting organics useful in polymer-based photodiodes and solar cells.

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1. Introduction

Since the late 1990s literature describing new organic and polymer-based photodiodes has started to appear. These devices are relatively inexpensive and straight-forward to construct and have shown significant potential in various applications [1,2]. The use of soluble conducting organic oligomers and polymers allows development of high throughput printing processes and integration on large and flexible substrates. In contrast, fabrication of state-of-the-art photodetectors based on inorganic materials such as silica is relatively expensive and suffers from limitations such as the necessity of stepwise vacuum depositions, high temperatures, and long process cycles. There is a developing interest for the use of inexpensive organic photodiodes in the field of radiation detection, including direct and indirect X-ray, alpha particle, and gamma-ray detection [3]. These may have important roles in ongoing worldwide efforts directed towards the detection and tracking of fissile materials used in weapons of mass destruction.

Since world fossil fuel production is expected to peak within the next several years, the development of specialty materials for renewable energy has also received emphasis. One of the most important renewable sources is solar power, which is clean and readily available. Silicon-based solar cells are considered to be the state of the art at present and have a relatively high efficiency, but, like inorganic photodiodes, they are expensive to manufacture [4]. Polymer-based solar cells are much less expensive but their energy conversion efficiencies are low [5]. Thus the development and incorporation of new materials that can raise their efficiencies is an important goal. Electrically conducting oligomers and polymers are one example of such materials. If they could be produced in simple, inexpensive processes their value in this application may be immense.

The objective of our work described below has been to develop novel oligomers or polymers of this type, having good electron-accepting and transporting properties (“n-dopable”) [6] that will be useful in polymer-based photodiodes and possibly solar cells, as well as organic field effect transistors (OFETs) [7] and organic light emitting diodes (OLEDs) [8]. Other newly emerging applications include conductive inks for low-cost printed circuit boards and chemiresistive sensors. It was desired that the oligomer or polymer be easy to synthesize (in few steps, or one step) and require inexpensive starting materials.

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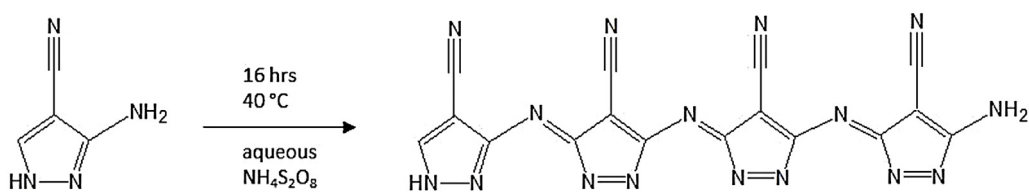


Fig. 1. One-step synthesis of oligo (APCN).

In our approach we used a simple pathway involving oxidative oligomerization of nitrogen-rich pyrazoles having primary amines. This was done in a manner similar to the synthesis of polyaniline, wherein the aniline amine group forms a bridge between each polymer repeat unit. To form oligomers that are electron-deficient, and thus likely to be n-dopable, we wanted to explore monomers that contained an electron-withdrawing group. To this end we chose 3-amino-1H-pyrazole-4-carbonitrile (“3AP-4CN”). This starting compound is shown in Fig. 1. At present it is sold commercially as a pharmaceutical intermediate [9] at the relatively very low cost of ~\$2.00/gram in bulk [10]. Thus our criteria for an inexpensive starting material were met. A one-pot synthesis of 3AP-4CN has been reported [11]. It should be mentioned that C₆₀ fullerene and its derivatives are often used as electron acceptors in polymer solar cells [12]. Currently, the cost of C₆₀ is ~\$20.00/gram in bulk (BuckyUSA, Inc.), a factor of 10 higher than 3AP-4CN. The C₆₀ derivatives are almost always expensive because of the multiple steps needed in their synthesis. In contrast, the oligomer product from 3AP-4CN is obtained in one step, as discussed below. We will refer to it as “oligo(APCN)”.

2. Experimental

Reagents were obtained from Sigma–Aldrich and used without further purification. UV–visible measurements were made with a Cary 5000 spectrometer, and fluorescence measurements made with a Fluoromax-3 (Horiba) fluorimeter. Infrared spectroscopy was performed using a Thermo Nicolet 870 FTIR. Cyclic voltammetry and EIS were performed using a CH Instruments 700D potentiostat. NMR was performed using a Varian 400 NMR Spectrometer (Agilent Technologies), with dimethyl sulfoxide-d₆ as solvent. Mass spectrometry was performed using a 5500 QTrap LC-Mass Spectrometer (Applied Biosystems), and an AB Sciex 5600-triple TOF instrument (AB Sciex) equipped with a DuoSpray ionization source/TIS electrospray probe. Samples were dissolved in 50% v:v methanol:water or 50% v:v deuterated methanol:deuterium oxide. Voltages were 5500 V in positive mode and –4500 V in negative mode. Photoirradiation was performed using an Oriel Model 66,001 Lamp (Newport, Ltd.).

The 3AP-4CN was oligomerized at 40 °C in a one-step process by using a near-stoichiometric amount of ammonium persulfate in acidic solution (pH 0.5–1.0) (Fig. 1). An acidic aqueous solution (“A”) with monomer was prepared, along with a second aqueous solution (“B”) with the ammonium persulfate oxidant. The two solutions were then mixed, and the reaction proceeded overnight at 40 °C. Solution A was prepared by adding 1.20 g monomer 3AP-4CN and 1.00 ml HCl to 30 ml DI water. Solution B was prepared by adding ammonium persulfate (APS, 3.0 g) to 30 ml DI water. The two solutions were then mixed, and the reaction was then allowed to proceed at 40 °C while stirring overnight, and it was then halted by raising the pH to 7.1 by adding aqueous 1.0 M NaOH. A solid precipitate formed, which was brick-red. It was dried under nitrogen at 75 °C and washed with DI water at 75 °C, and allowed to dry again under nitrogen at RT. It was washed once again with DI water at 75 °C, dried overnight under vacuum and

stored at RT. The overall yield was 57%. Optimization of synthesis conditions should give improved yields.

For the photocurrent studies, photocells were constructed using standard droplet deposition methods. The oligo(APCN)/POTP blend (see Section 3) was formed by dissolving the former in chloroform (4 wt% polymer), and the latter in pyridine (4 wt % oligomer). After heating to 80 °C for 15 min, the two solutions were vigorously mixed and the resulting solution was drop-cast onto a pre-heated (80 °C) gold-coated silica support and allowed to dry at that temperature overnight. Next, the PEDOT-PSS was cast onto ITO-coated silica and also allowed to dry at 80 °C overnight. The cell was fabricated by first introducing the ionic liquid/propylene carbonate (PC) mixture (see Section 3) onto the POTP film as a droplet, then placing the PEDOT-PSS coated ITO onto the silica/gold/oligo(APCN)/POTP blend/ionic liquid/PC construction. The sandwich-type construction was then clamped together. The combined thickness of the PEDOT-PSS film, the ionic liquid-PC, and the OAPCN layers was ~150 microns. The thickness distribution was as follows – PEDOT-PSS, 24 ± 4 microns; ionic liquid/PC, 40 ± 4 microns; OAPCN/POTP, 83 ± 5 microns.

The working electrode was interfaced to the gold/oligo(APCN)/POTP blend and the counter and reference electrodes were interfaced to the PEDOT-PSS-ITO hole-transporting layers. During the photocurrent measurements, the current was monitored as a function of time. During these experiments the sample was held at either at zero voltage or various biases ranging from –0.6 V to +1.0 V.

For cyclic voltammetry of oligo(AP-CN), the electrolyte was 100 mM tetrabutyl ammonium hexafluorophosphate (TBAPF₆) in DMF, deaerated. For impedance spectroscopy, the electrolyte was 100 mM tetrabutyl ammonium hexafluorophosphate (TBAPF₆) in acetonitrile, deaerated. A glassy carbon working electrode was used with an Ag/AgCl reference electrode.

3. Results and discussion

The formal chemical name of oligo(APCN), generated by ACD/ChemSketch 2012, is 5-amino-3-(((3Z)-4-cyano-3-(((3Z)-4-cyano-

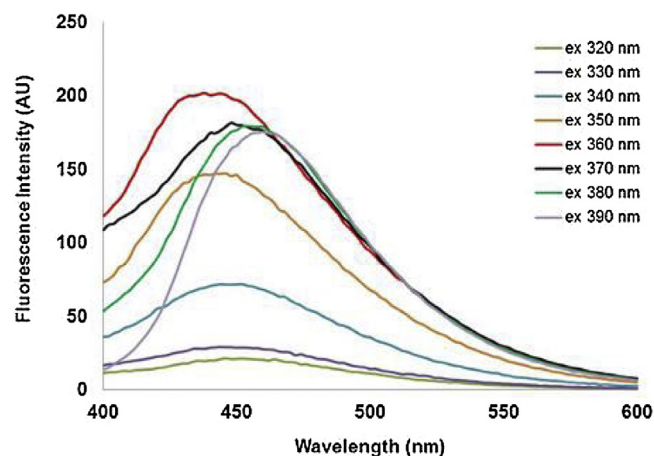


Fig. 2. Fluorescence spectra of oligo(AP-CN) in DMF.

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