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Multifunctional polymers for electrochromic, memory device, explosive detection and photodetector: Donor-acceptor conjugated isoindigo derivatives with strong fluorescence

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ABSTRACT

We report here that a series of novel donor-acceptor (D–A) conjugated polymers based on isoindigo were synthesized and characterized. As novel electrochromic materials, their optical and electrochemical properties have been investigated. Cyclic voltammograms (CV) of the polymer films exhibit two pairs of obvious redox peaks in the range of 0.76–1.80 V with strong color changes in the visible and near infrared (NIR) regions. The coloring and bleaching time are in the range of 3.5–4.9 s and 4.4–5.0 s, respectively. The amount of char yield at 800 °C in nitrogen for polymers was in the range of 56–64%. Especially, the polymers show strong fluorescence with a fluorescence quantum efficiency (Φ_{PL}) of up to 32.5% which is reported firstly. In addition, memory properties, explosive detection and photoelectric properties for polymers are studied which indicating promising results.

1. Introduction

At present, many new electrochromic materials have been developed by scientists and have attracted worldwide attention [1,2]. Electrochromic materials play an irreplaceable role in smart windows, electronic paper, electrochromic display devices, camouflage materials [3]. These advantages of the polymer (solution processability, large area fabrication and stretchable, collapsible capability) make them the best choice for electrochromic materials [4]. On the other hand, polymer-based electrochromic materials have fast response time, high optical contrast, properties through structural control and mechanical deformation [5]. According to previous related reports, Liou and Hsiao's groups have made great progress in the research of electrochromic materials based on triphenylamine (TPA) derivatives and polymers [6–9]. TPA derivatives and polymers due to unique chemical structure make them excellent in thermal stability, electron transport, and hole mobility [10].

The polymers containing TPA derives can keep oxidized states without applied potentials during long time. And the potentials and colors in oxidized states can be modulated by modifying the structure of the TPA derives in main chain or side groups. As the designing idea and pioneering work of Wei Huang for D-A polymers used in OLED devices, conjugated polymers comprising of alternating electron donor (D) and acceptor (A) units in the backbone ave attracted considerable attention due to narrow band-gaps and its energy levels can be controlled [11–14]. The forming intramolecular D-A structures is a very successful strategy for enhanced electronic properties and improved device performances [15,16]. We can select different comonomers into the main chain to regulate the energy gap of the polymers.

Isoindigo is a well-known organic pigment that contains two strong electron-withdrawing lactam rings [17–19]. So isoindigo-based polymers shows strong light absorption and strong electron-withdrawing ability, low HOMO levels, photochemical stability, relatively small bandgaps [20,21]. In recent years, they have become darlings in the research of solar cells, high-performance organic photovoltaics (OPVs) and organic field-effect transistors (OFETs) [22,23]. Relevant literature reports show that there are a great deal of research interest in isoindigo for D-A conjugated polymers [24,25].

Based on the above theory, we designed and synthesized four isoindigo-based D–A type conjugated copolymers (**P1**, **P2**, **P3** and **P4**)

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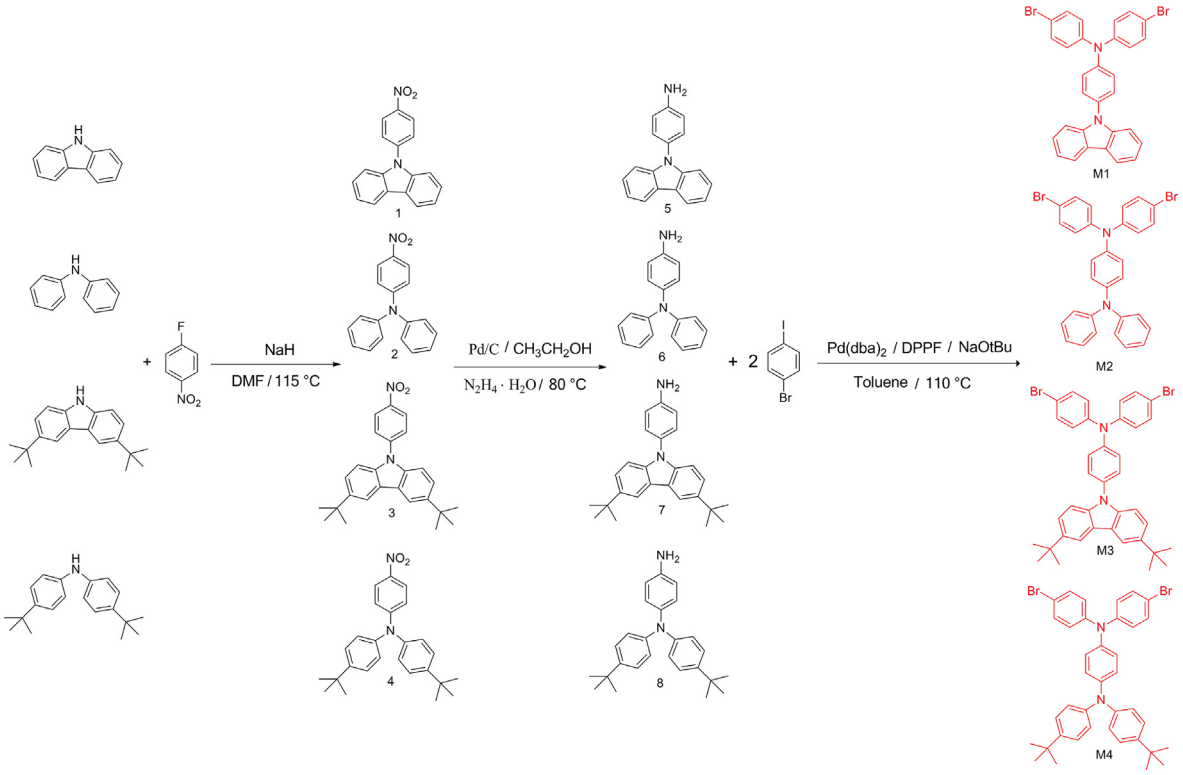
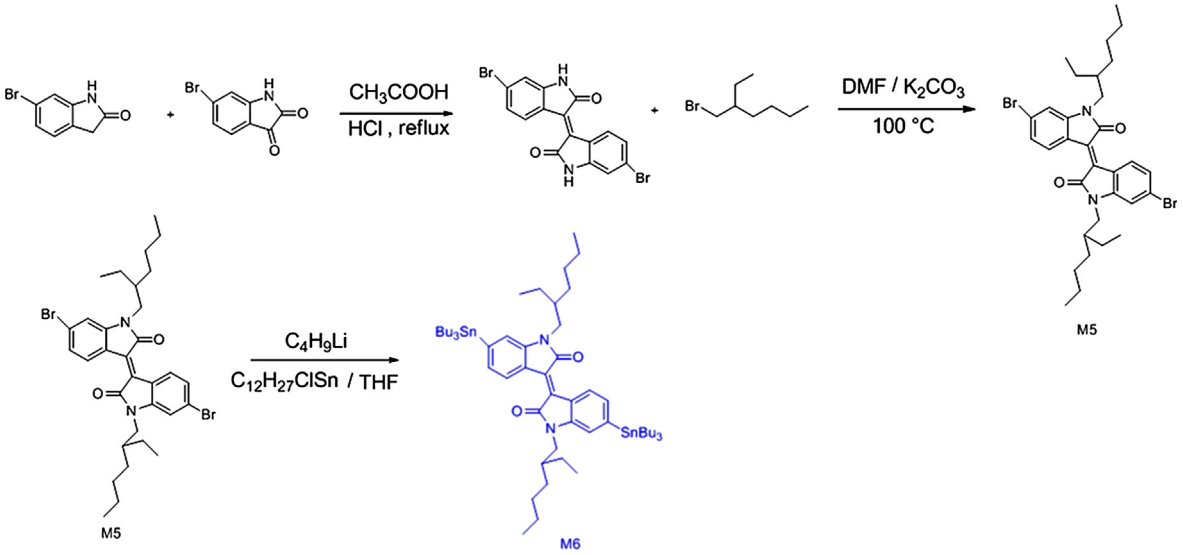


Scheme 1. Synthetic route to the diamine monomer **M1-M4**.



Scheme 2. Synthetic route to the diamine monomer **M6**.

with four different TPA derivatives and investigated their electrochromic properties and other properties. Interestingly, the polymers show strong fluorescence contrast to most reported D-A polymers. Among them, three polymers show satisfactory electrochromic properties with relatively high coloration efficiency (CE; η) in the range of 91–114 $cm^2\ C^{-1}$. Scientists anticipate one material has many functions which can endow arficial skin many properties, such as being sensitive to thermol, optical, pain stimulus and integrate them in one chip. So we try to develop the other function of the polymers. We also study the memory performance of the fabricated devices. The current ratio of the device is as high as 1×10^4, which displaying attractive potential applications in the field of memory devices. As a fluorescent sensor, these polymers show highly sensitive detection of nitroaromatic explosives. In order to gain insight into the polymer, we systematically studied the thermal, organic solubility, optical, electrochemical, optoelectronic and electrochromic properties of the polymer.

2. Experimental

2.1. Synthesis of monomers

The compounds including **M1, M2** and **M5** were synthesized according to literature procedures [26–28]. **M3, M4** and **M6** are reported by our groups. The detailed synthesis process is shown in Schemes 1 and 2.