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A neutral state colorless phosphazene/carbazole hybride dendron and its electrochromic device application

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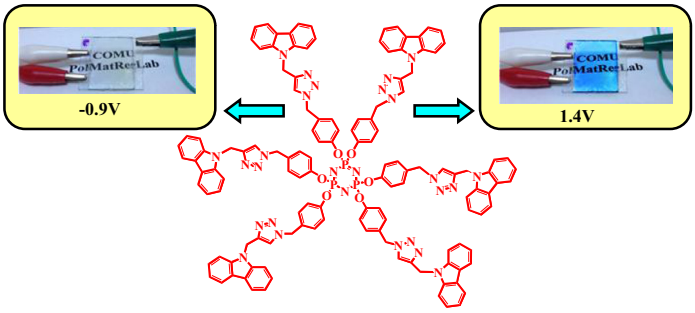
HIGHLIGHTS

- A new phosphazene/carbazole hybride dendritic network was synthesized.
- A neutral state colorless electrochromic device was constructed.
- The device has a short response time, high coloration efficiency and redox stability.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, a new phosphazene/carbazole hybride dendron (**PC**) was synthesized and then directly coated onto ITO glass surface to provide a dendritic polymer network, **poly**-(**PC**), by using potentiodynamic electrochemical process. Structure of dendron was identified by FT-IR, ^{1}H and ^{31}P NMR, and also TOF-MS analyses. The optical and electrochemical properties of PC and its electrochemical cross-linked product were investigated by using UV–vis absorption, fluorescence and CV techniques. A neutral, colorless electrochromic device was constructed in the sandwich configuration [indium tin oxide (ITO)-coated glass/anodically coloring material (poly-(PC))//gel electrolyte//cathodically coloring material (PEDOT)/ITO-coated glass] and revealed a short response time (about 0.5 s), high coloration efficiency (981 $cm^2\ C^{-1}$) and high redox stability.

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1. Introduction

Electrochromism is a phenomenon present in some materials of reversibly varying color when potential is applied to such material. Formation of new absorption bands at different wavelengths of the visible and/or NIR regimes while switching between oxidation/reduction states induces this phenomenon. First, inorganic semi-conductors such as tungsten trioxide (WO_3) and iridium oxide (IrO_2) were commonly used as electrochromic materials [1–3], but then conducting polymers received great attention for electrochromic technology [4–6] due to easily tunable band gap and also neutral state colors. The most popular commercial applications of electrochromic materials are smart windows, switchable mirrors and displays [7–11].

Carbazole is known to be both an electron-donating (p-type) chromophore and also an effective short wavelength emitter

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[12]. Carbazole can be easily functionalized at (3,6) [13,14], (2,7) [15,16] or N-positions [17]. Due to this useful property, it can be easily used in polymeric systems, both in the main chain as building blocks and in a side chain as subunits. Therefore the conjugated polymers containing carbazole moiety have received great attention for optoelectronic technology in the last three decades [18]. These polymers can be used in light emitting diodes, electroxerography, microcavity photoconduction, electrochromic and photovoltaic devices [12]. Moreover, poly(3,6-carbazole)s demonstrate remarkable electrochromic properties owing to the conjugation breaks which are present due to the insertion of a 3,6-linkage. Reynolds et al. proposed one of the remarkable multicolored polymer systems that is based upon this property of poly(3,6-carbazole)s [19]. Because of broken conjugation, these polymers generate polarons which are separated from one another and do not combine [5,19,20]. Upon further scan at higher potentials in the anodic regime, another electron is removed, providing bipolarons. Owing to these important properties, poly(3,6-carbazole)s based electrochromic materials have multiple colors with separate colors present for the neutral, polaronic, and bipolaronic species at various oxidation states [21]. Another significant behavior of poly(3,6-carbazole)s in electrochromic materials is neutral state colorless property [22–24]. To obtain a colorless and transparent state, these types of materials do not need any potential or energy. Because of this significant property, poly(3,6-carbazole)s have received great attention for electrochromic technology such as smart windows [25,26].

Cyclic phosphazenes contain a non-delocalized planar ring containing —P=N— units. Thanks to these features, they are very interesting class of compounds for the synthesis of dendrimeric materials [27]. Phosphazene compounds, both cyclic and linear, have been extensively used in the preparation of functional materials due to their properties such as biocompatibility, biodegradability, non-toxic degradation products [28], liquid crystalline [29] and flame retardant behaviors [30]. These structures gain some useful properties owing to the phosphazene core. A fully substituted cyclotriphosphazene core is very stable in aggressive chemical conditions [31]. The preparation of a functional cyclotriphosphazene core is fairly simple due to easy substitution of halogen atoms in the structure of hexachlorocyclotriphosphazene with nucleophiles such as alcohols, amines and phenols [32]. Besides, the cyclotriphosphazene ring is inert and the optical and electronic properties of the prepared material depend on the functional groups of dendron [31]. In the recent years, dendrimeric compounds with cyclotriphosphazene cores have been used as the active layer in organic optoelectronic devices [33–36]. Solution processable phosphorescent dendrimers with cyclotriphosphazene core and carbazole functionalized cyclotriphosphazene compounds have been synthesized and successfully used for OLED application by Bolink et al. [37] and Soh et al., respectively [38]. In addition, Gorur et al. has carried out electrochromic device application of a thiophene functionalized star polymer containing a cyclic phosphazene core [39].

In this work, we synthesized a new phosphazene/carbazole hybride dendron (PC) to use in a neutral colorless electrochromic device. The dendritic polymer film of **PC** was obtained by using potentiodynamic electrochemical deposition. The characterization of the monomer and corresponding polymer were performed via several techniques such as ^{1}H and ^{31}P NMR, TOF-MS, Fourier transform infrared (FTIR) spectroscopy, cyclic voltammetry (CV), UV–vis and florescence spectroscopy. The colorless **poly**-(**PC**) film converted to green color after positive potentials were applied. It is a big advantage for electrochromic materials due to in the present applications. All ideal RGB electrochromic materials can be turned into transmissive upon oxidation. To have the smart window transparent when needed, the electrochromic material must be continuously kept at its oxidized state, and it is switched between transmissive and different states for coloration (red, green, and blue) [40]. It is obvious that keeping electrochromic material under potential to have its transmissive form means the device continuously uses energy, which causes the deterioration of the electrochromic material. **Poly**-(**PC**) is transparent at its neutral state and has a very high value of optical transmittance (>90%), which decreases to about 45% ($\Delta T\% = 51\%$) upon only scanning from 0 to 1.4 V. Moreover, it is realized that phosphazene unit substituted to carbazole to obtain dendritic structure gains useful properties for electrochromic applications such as high stability, coloration efficiency and low response time. Further, the constructed electrochromic device based on **poly-PC** as anodically coloring and poly(3,4-ethylenedioxythiophene) (PEDOT) as cathodically coloring materials can be switched between colorless and cyan. This device has important properties such as colorless neutral state, as well as a high coloration efficiency (981 $cm^2\ C^{-1}$), a very short response time (about 0.5 s), and a high redox stability. In summary, it is very clear that it can be accounted as a promising material to be used in smart window applications because of this dual behavior.

2. Experimental

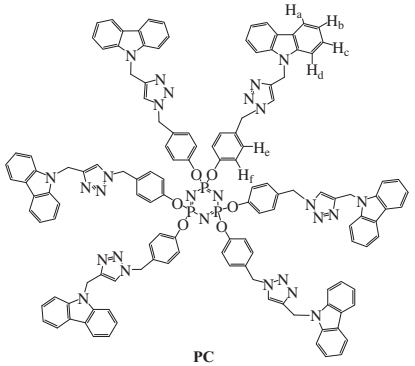
2.1. Materials

All chemicals were purchased from Aldrich Chemicals and used without further purification. Compounds **1** [32] and **2** [41] were prepared using previously reported procedures.

2.2. Synthesis of PC dendron

To an argon-saturated solution of compound **1** (0.1024 g, 0.10 mmol), compound **2** (0.147 g, 0.72 mmol) and N,N′,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA, 0.25 mL, 1.20 mmol) in dry THF (25 mL), and copper(I) iodide (0.0114 g, 0.06 mmol) was added. The reaction was stirred at 60 °C for 12 h under inert atmosphere. At the end of this time, the solvent of the reaction mixture was evaporated by rotary evaporator. A pale yellow solid was obtained from purification of the residue using column chromatography on silica gel with $CHCl_3$/methanol (9:1) solvent mixture (0.213 g, 94.4%): mp 143–144 °C.

FT-IR (cm^{-1}): 3052 (C—H aromatic), 2929 (C—H aliphatic), 1595 (C=C aromatic), 1154 (P=N), 955 (P—O—C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97–7.99 (d, 12H, Ar—$H_{aa'}$) 7.32–7.36 (m, 24H, Ar—$H_{dd'}$ and Ar—$H_{cc'}$); 7.17–7.14 (m, 12H, Ar-$H_{bb'}$); 7.07 (s, 6H, triazole CH); 6.54–6.56 (d, 12H, Ar—$H_{ee'}$); 6.44–6.46 (d, 12H, Ar—$H_{ff'}$); 5.45 (s, 12H, —N—CH_2—N); 4.95 (s, 12H, —N—CH_2—Ar). ^{31}P NMR (202 MHz, $CDCl_3$, 25 °C): 8.30. TOF-MS *m/z* Calcd for $C_{132}H_{102}N_{27}O_6P_3$: 2255.320 Found: 2255.838.



PC

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