Donor−Acceptor Polymer with Benzotriazole Moiety: Enhancing the Electrochromic Properties of the "Donor Unit"

Abidin Balan, Gorkem Gunbas,[†] Asuman Durmus, and Levent Toppare*

Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey

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A new donor−acceptor type polymer poly(4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2-dodecyl-2H-benzo [1,2,3] triazole) (PBEBT) was synthesized and its electrochromic properties were investigated. Spectroelectrochemistry studies for PBEBT showed an absorption maximum at 618 nm which is nearly identical to that of poly(ethylenedioxythiophene) (PEDOT) where polymer has a saturated blue color in its neutral state. However, PBEBT film revealed better properties than that of PEDOT in terms of optical contrast, switching time and coloration efficiency. Additionally, electrochemical and spectral results conclude that PBEBT is a both p- and n-type dopable polymer. PBEBT proved to be a superior option for electrochromic display device applications.

Introduction

Conjugated polymers have aroused a great attention after their discovery[1] because these materials are potentially useful for many applications especially in solar cells,[2] LED's,[3] field effect transistors,[4] sensors,[5] and electrochromic devices.[6] Electrochromic materials possess the ability to reversibly change color by altering their redox state. Optically responsive conducting polymers that reveal electrochromism are significantly inquired for their potential use in commercially important technologies like data storage and display devices.

Low band gap polymers are greatly desired for electrochromic applications since they can be utilized as cathodically coloring polymers with highly transmissive oxidized states.[7,9c] Also, degradation effects due to the redox switching are greatly reduced with the use of these materials since the polymer oxidation and reduction were achieved at lower potentials.[8] There are number of methodologies for the synthesis of narrow band gap polymers, namely reduction of bond-length alternation, synthesis of highly planar systems, and alteration of interchain and resonance effects. Besides these methods, donor−acceptor approach was commonly applied for reducing the band gap and avoiding solubility problems.[9] This type of polymer leads to narrower band gaps because of the mesomeric effects, which enable a double bond character between the donor and acceptor units.[10]

Thiophene- and pyrrole-based polymeric materials are great candidates for electrochromic device applications because of their stabilities, high contrasts, and fast switching times.[11] Among these materials, 3,4-alkylenedioxythiophenes were proven to be excellent candidates as electrochromic materials.[12] One of the famous electrochromic material, poly-3,4-ethylenedioxythiophene, was known as the blue component for realization of RGB-based display devices. It was also utilized as a building block for synthesis of many advanced materials. PEDOT reveals a unique combination of moderate band gap and low oxidation potential, which resulted in a exceptionally stable, highly conductive polymer that also exhibits excellent optical transparency in the visible region.[13]

In this report, we highlight the synthesis of a novel donor−acceptor type polymer bearing EDOT as the donor and benzotriazole as the acceptor unit. The unique donor−acceptor

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* Corresponding author. Fax: 90 312 210 32 00. Tel: 90 312 210 32 51. E-mail: toppare@metu.edu.tr.

[†] Current address: Department of Chemistry, University of California, 1 Shields Avenue, Davis, CA 95616.

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match in poly-4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2-dodecyl-2H-benzo [1,2,3] triazole (PBEBT) resulted in a polymer which revealed superior electrochromic properties than the pristine EDOT in terms of optical contrast, switching time, and coloration efficiency. These striking preliminary results are given in this report.

Experimental Section

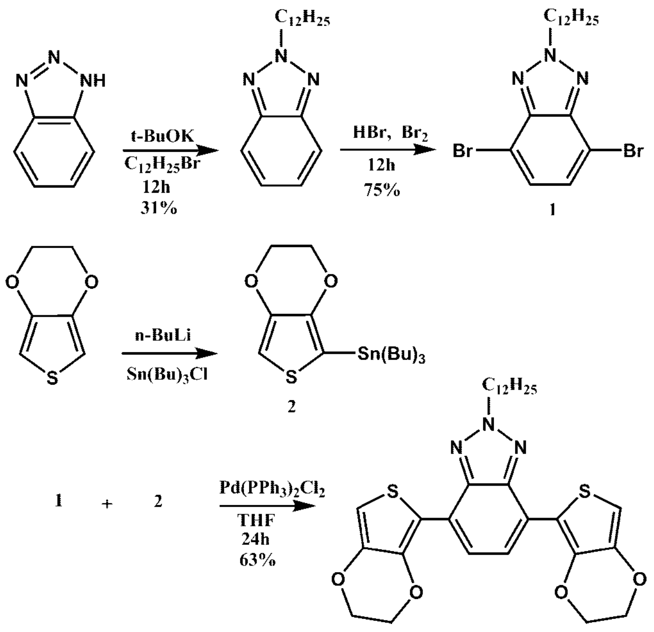
General. All chemicals were purchased from Aldrich except anhydrous tetrahydrofuran (THF) which was purchased from Acros. Tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane was synthesized according to previously described method[14] Electropolymerization was performed with a Voltalab 50 potentiostat in a three-electrode cell consisting of platinum wire or indium tin oxide (ITO) coated glass as the working electrode, platinum wire as the counter electrode, and an Ag wire as the pseudo reference electrode. Electrodeposition was performed from a 0.1 M solution of $TBAPF_6$ at a scan rate of 100 mV/s for 35 cycles. UV−vis−NIR spectra were recorded on a Varian Cary 5000 spectrophotometer at a scan rate of 2000 nm/min. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Spectrospin Avance DPX-400 apectrometer and chemical shifts were given relative to tetramethylsilane. Colorimetry measurements were performed via Minolta CS-100 apectrophotometer. Mass analysis was carried out on a Bruker time-of flight (TOF) mass spectrometer with an electron impact ionization source.

Synthesis. *Synthesis of 2-Dodecylbenzotriazole.* Synthesis of 2-dodecylbenzotriazole was performed according to methodology described in the literature for a similar compound.[15] 1,2,3-Benzotriazole (5.0 g, 42 mmol), potassium tert-butoxide (5.0 g, 44 mmol), and bromododecane (12.2 g, 49 mmol) were dissolved in methanol (50 mL). The reaction mixture was refluxed for 12 h and monitored by TLC. After removal of the solvent by evaporation, the residue was dissolved in $CHCl_3$ and extracted with water. The organic extract was dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The residue was subjected to column chromatography(3:2 chloroform:hexane; R_f, 0.29) to obtain 2-dodecylbenzotriazole as a colorless oil (3.7 g, 31%). ^1H (400 MHz, $CDCl_3$, δ): 7.76 (m, 2H), 7.26 (m, 2H), 4.62 (t, $J = 7.1$ Hz 2H), 2.12 (m, 2H), 1.25−1.15 (m, 18H), 0.78 (t, $J = 6.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl3, δ): 144.3, 126.1, 117.9, 56.6, 31.8, 30.0, 29.5, 29.4, 29.4, 29.3, 29.3, 29.0, 26.5, 22.6, 14.0.

Synthesis of 4,7-Dibromo-2-dodecylbenzotriazole. Synthesis of 4,7-dibromo-2-dodecylbenzotriazole was performed according to a method described for a similar compound.[15] 2-Dodecylbenzotriazole (3.7 g, 13.1mmol) and an aqueous HBr solution (5.8 M, 15 mL) were added to a flask, and the mixture was stirred for 1 h at 100 °C. Bromine (5.9 g, 36 mmol) was added, and the mixture was stirred for 12 h at 135 °C. After the mixture was cooled to room temperature, an aqueous solution of $NaHCO_3$ was added and the product was extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. With column chromatography(1:1 chloroform:hexane; R_f, 0.33), 4,7-dibromo-2-dodecylbenzotriazole was obtained as light yellow oil (4.3 g, 75%). ^1H (400 MHz, $CDCl_3$, δ): 7.36 (s, 2H), 4.60 (t, $J = 7.0$ Hz, 2H), 2.10 (m, 2H), 1.38−1.12 (m, 18H), 0.80 (t, $J = 6.9$ Hz, 3H). ^{13}CNMR (100 MHz, $CDCl_3$, δ): 143.7, 129.4, 109.9, 57.4, 31.8, 30.1, 29.5, 29.5, 29.4, 29.4, 29.3, 28.9, 26.4, 22.6, 14.0.

Synthesis of 4,7-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2-dodecyl-2H-benzo [1,2,3] Triazole (BEBT). 4,7-Dibromo-2-dodecylbenzotriazole (100 mg, 0.224mmol) and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)stannane were dissolved in anhydrous THF (100 mL), the solution was purged with argon for 30 min and dichlorobis(triphenylphosphine)-palladium(II) (50 mg, 0.045 mmol) was added at room temperature under an argon atmosphere. The mixture was refluxed for 24 h. Solvent was evaporated under a vacuum and the crude product was purified by column chromatography (2:1 chloroform:hexane; R_f, 0.45) on silica gel to obtain 80 mg (63%) BEBT. ^1H (400 MHz, $CDCl_3$, δ): 8.00 (s, 2H), 6.40 (s, 2H), 4.60 (t, $J = 7.0$ Hz, 3H), 4.40(m, 4H), 4.22(m, 4H), 2.10 (m, 2H), 1.38−1.12 (m, 18H), 0.80 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 141.6, 140.7, 139.8, 122.8, 120.6, 112.3, 101.2, 64.9, 64.0, 56.1, 31.2, 29.1, 28.9, 28.8, 28.8, 28.7, 28.6, 28.2, 25.8, 22.0, 13.9. MS (m/z): 567 [M^+].

Scheme 1. Synthetic Route to Monomer BEBT



Results and Discussion

Monomer Synthesis. The design and synthesis of the monomer was crucial to control the electrochromic properties of the resultant polymer (scheme 1). Although the overall yield is quite satisfactory, because of the two possible alkylation sites of the benzotriazole,[15,16] the desired isomer was isolated in 31% yield in the first step of the reaction sequence. However, this reaction stands as a practical step with relatively cheap starting materials and reagents; hence it can be performed in quite large scales. The bromination and coupling steps revealed satisfactory yields. Since alkyl substitution to polymeric backbone is highly effective in enhancing the optical and physical properties of the polymer,[17] derivatization of benzotriazole unit with substituents allows us to modify the outcome of the electrochromic properties of the polymer.[18] The available alkylation site is valuable to synthesize soluble polymers both in organic and aqueous media. The dodecyl group was inserted in the structure to improve the solubility of the monomer which eases the characterization. The dodecyl group was apparently not sufficient enough to generate a soluble polymer in our case.

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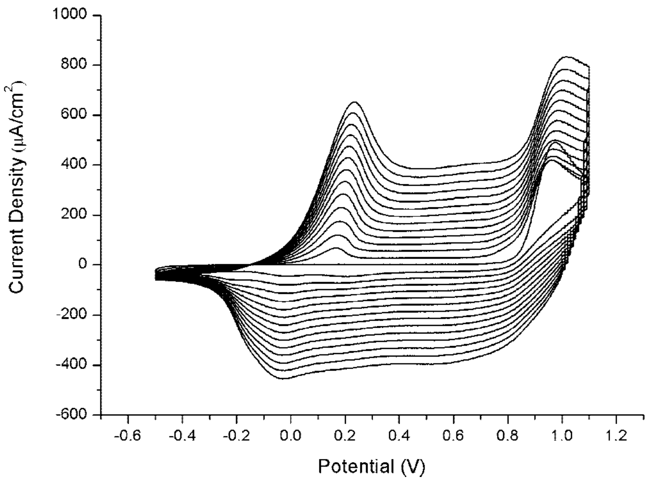

Figure 1. Repeated potential scan electropolymerization of BEBT at 100 mV s^{-1} in 0.1 M TBAPF$_6$/CH$_2$Cl$_2$/ACN on an ITO electrode.

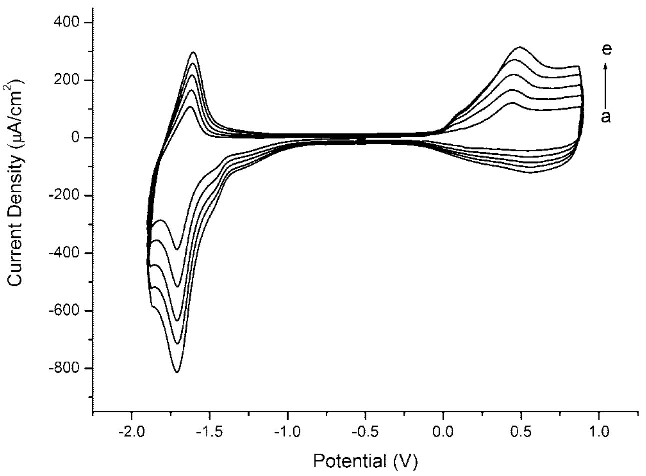

Figure 2. Scan rate dependence of a PBEBT film in TBAPF$_6$/ACN: (a) 100, (b) 150, (c) 200, (d) 250, and (e) 300 mV s^{-1}.

However, many other longer alkyl chains or branched alkyl chains may result in soluble conducting polymers[9b] bearing a benzotriazole unit in the backbone. In addition, long ethylene glycol chains in the backbone of the polymer would result in water soluble derivates of this novel donor−acceptor type polymer. The results of the synthesis and properties of the soluble derivatives will be discussed in future works.

Electropolymerization. Multiple scan voltammetry on ITO was performed in a 0.1 M TBAPF$_6$ and 1×10^{-2} M BEBT solution applying potentials between −0.5 V and +1.1 V at a scan rate of 100 mV/s (Figure 1). The solvent was chosen as a mixture of acetonitrile(ACN) and CH$_2$Cl$_2$ (95/5, v/v) because of the poor solubility of the monomer in ACN. On the other hand, because the monomer bears an alkyl chain in the structure, the oligomers are soluble in pure CH$_2$Cl$_2$. Hence a mixture of these two solvents was applied as the solvent system. The monomer oxidation potential was observed at 0.97 V, which is quite lower than the oxidation potential of EDOT. After the first cycle, an oxidation peak at 0.23 V and its reverse cathodic peak at −0.04 V appeared.

The polymer also revealed n doping properties where a reversible redox couple with an E_{ox} of −1.62 and E_{red} of −1.71 V, versus the same reference electrode, was observed for the n type doping and dedoping processes respectively (Figure 2). PBEBT film is saturated blue (*Y*, 195, *x*, 0.209; *y*, 0.216) in its neutral state, and the color changes to highly transparent light blue (*Y*, 688; *x*, 0.288; *y*, 0.330) in the oxidized state. The anodic and cathodic peaks of PBEBT showed were proportional with the scan rate, which indicates that the films were well-adhered and charge transfer process was not dominated by diffusion.[8]

Spectroelectrochemistry. To probe the optical changes upon doping, spectral changes were investigated by UV−vis−NIR spectrophotometer in a monomer free, 0.1 M TBAPF6, ACN solution while increasing the applied potential from −0.5 to 1.1 V.

Although PBEBT is a donor−acceptor type polymer and this type of materials usually show two distinct absorption maxima,[19] PBEBT revealed only one because of the dominant donor characteristic of the EDOT moiety (Figure 3). The peak at 618 nm which corresponds to the $\pi-\pi^*$ transition of the neutral polymer is analogous to EDOT itself. Hence, the polymer is deep blue in the neutral state. The band gap of the polymer is 1.6 eV, which was calculated from the onset of the $\pi-\pi^*$ transition.

As a result of charge carrier formation upon oxidation, the absorption in the visible region depletes and new absorption bands evolve at 900 nm and 1600 nm representing the formation of polaronic and bipolaronic bands.[20]

Although conducting polymers have great tendency to exhibit both p- and n-doping ability,[21] only a few of them show this notable property. The n-type polymers can be used in fabrication of many different types of polymer based electronic devices such as bipolar and pnp type field effect transistors.[22] True n-type doping process can be proved by a reversible redox couple at negative potentials and additionally and more importantly, a drastic change in the NIR region upon reduction. As seen from Figure 4, PBEBT reveals a drastic change of 30% in optical contrast upon reduction which is a critical proof that PBEBT is a true n-type dopable polymer.[23] The polymer had a pale bluish-gray (*Y*, 615, *x*, 0.298; *y*, 0.314) in the reduced state.

Kinetic Studies. Electrochromic switching studies were performed to monitor the percent transmittance changes as a function of time and to determine the switching time of the polymer at its λ_{max} by stepping potential repeatedly between the neutral and oxidized states. PBEBT revealed exceptional optical contrasts of 53% at 618 nm and 71% at 1600 nm (Figure 4). PEDOT has 44% optical contrast at around 600 nm. These optical contrast data for PBEBT are surprisingly better than the ones observed for PEDOT.[12c] Additionally the PBEBT showed remarkable switching time of 1.1 s at 100% optical contrast where PEDOT needs at least 2.2 s to achieve full switching (Table 1).This argument is true even for a PBEBT film with an optical contrast greater

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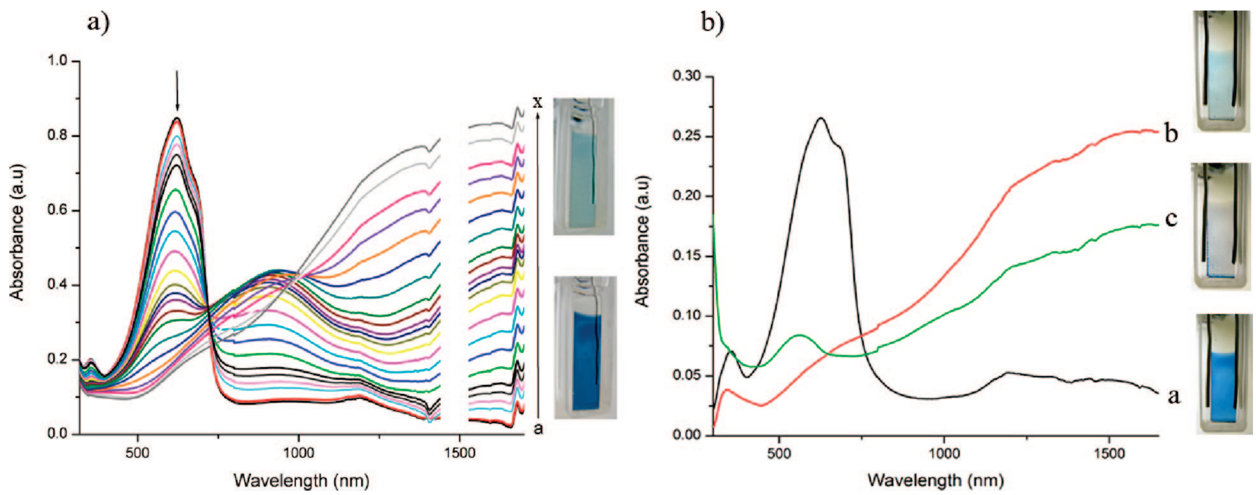

Figure 3. Spectroelectrochemistry of PBEBT film on an ITO coated glass slide in monomer-free, 0.1 M $TBAPF_6$/ACN electrolyte-solvent couple at applied potentials (V). (a) p-Doping; (a) −0.5, (b) −0.4, (c) −0.3, (d) − 0.2, (e) −0.1, (f) 0.0, (g) 0.1, (h) 0.15, (i) 0.2, (j) 0.25, (k) 0.3, (l) 0.35, (m) 0.4, (n) 0.45, (o) 0.5, (p) 0.55, (q) 0.6, (r) 0.65, (s) 0.7, (t) 0.75, (u) 0.8, (v) 0.9, (w) 1.0, and (x) 1.1. (b) n-Doping: (a) − 0.5, (b) 1.1, and (c) −1.71 V.

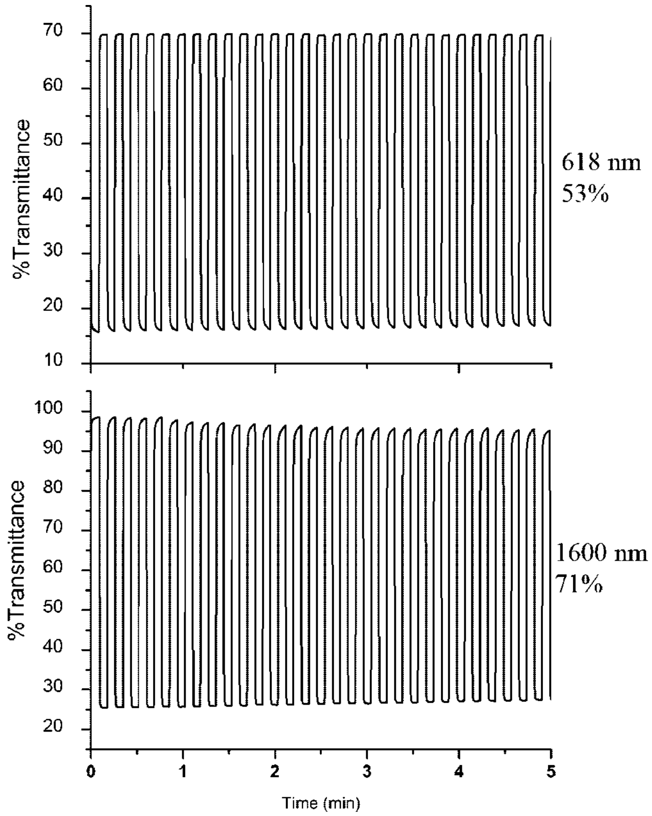

Figure 4. Electrochromic switching and percent transmittance change monitored at 618 and 1600 nm for PBEBT in 0.1 M $TBAPF_6$/ACN.

Table 1. Optical Contrast and Switching Time Comparison between PBEBT and PEDOT

	PBEBT (618nm)	PEDOT(610 nm)
optical contrast (%)	53	44
switching time (s)	1.1	2.2

than that of PEDOT. The coloration efficiency, which provides information about the contrast ratio acquired for a certain amount of charge introduced in the material is calculated as 211 cm^2/C (at 95% of full switch at 600 nm). It is the ratio between the change in optical density at a specific dominant wavelength and the injected/ejected charge per unit area of the electrode. As regards to the coloration efficiency PBEBT is remarkably higher than the coloration efficiency of PEDOT (183 cm^2/C).[24]

The long-term switching stability is a vital requirement toward many electrochromic device applications, especially smart windows.[25] To determine the stability of the polymer, a film was deposited on a Pt wire using cyclic voltammetry (CV) from a solution of 0.01 M monomer in 0.1 M $TBAPF_6$/CH_2Cl_2 electrolyte. The polymer films cycled between their fully neutral and oxidized states in lithium perchlorate/propylene carbonate (PC) electrolyte/solvent couple. Once electrochemical equilibration was reached (after 600 cycles), PBEBT revealed outstanding redox stabilities upon cycling, where less than 6% decrease in total charge was observed even after 4000 cycles, indicating the robustness of PBEBT upon successive switchings.

Conclusion

The presence of benzotriazole unit in the polymer backbone exceptionally enhanced the electrochromic properties of the “donor polymer”, namely, PEDOT. The optical contrast of the polymer was nearly 10% higher than that of PEDOT, whereas the switching time was found to be the half of the value for PEDOT. The stability of polymer was at least as remarkable compared to the “donor polymer”. The ease of synthesis with relatively high yields makes this polymer the paramount choice in RGB based device applications as the blue leg component. Benzotriazole is an exceptional acceptor group for the donor−acceptor type polymer synthesis and probably still hides many other interesting features. Synthesis of a solution processable derivative of this polymer and novel donor−acceptor type polymers bearing thiophene and selenophene units as the donor moiety will be the targets in near future.

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