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A novel electrochromic polymer containing triphenylamine derivative and pyrrole

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ABSTRACT

A novel conducting polymer was successfully synthesized via electropolymerization of N^1,N^4-bis(4-(1H-pyrrol-1-yl)phenyl)-N^1,N^4-diphenylbenzene-1,4-diamine (DPTPA). This polymer film exhibited six various colors under different potentials. Besides, this polymer film showed high optical contrast (41% at 852 nm, 52% at 617 nm) and fast switching time (1.3 s at 410 nm, 1.4 s at 852 nm and 0.6 s at 617 nm). Cyclic voltammogram and electro-optical study showed that the polymer film has a stable and well-defined reversible redox process as well as electrochromic behavior.

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1. Introduction

One of the most attractive properties of electrochromic (EC) materials would be multicolor display [1]. As a class of important EC material, conjugated polymers have received significant attention throughout the course of the past two decades because of their promising applications in light-emitting diodes, optical displays, electrochromic devices and analytical sensors [2–6]. The most important features of conjugated polymers are the possibilities to fine-tune the color through chemical structure modification of the conjugated backbone and to get multichromism from the same material [7].

Recently, triphenylamine (TPA) derivative materials, including small molecules and macromolecules, have been extensively investigated for hole transporters [8], light emitters [9–11], and polymer electronic memories [12]. TPA can also be considered as a good electrochromic material as it easily oxidizes to form radical cation with a noticeable change of coloration [13–15]. But Adams and coworkers reported that TPA could be easily dimerized to form tetraphenylbenzidine during the anodic oxidation pathway [16]. For electrochromic materials, this dimerization could be considered as an undesired side reaction, which might cause irreversible defect after several redox switches. To avoid this behavior, incorporating electron-donating substituents such as alkyl or alkoxy group at the para-position of the TPA group could prevent the coupling reactions and afford stable cationic radicals with lower potential [17]. Since polypyrrole was first electrochemically synthesized more than two decades ago by Diaz et al. [18], it has been intensively investigated. The superiority of the intrinsic properties of polypyrroles such as ease of synthesis, good redox properties, stability in the oxidized form, ability to give high electrical conductivities and useful electrical and optical properties make them certainly one of the most widely studied organic conducting polymers [19–21]. The combination of a TPA derivative and pyrrole was expected to obtain an excellent multicolor polymer containing both the advantages of TPA and pyrrole.

In this report, we successfully prepared a monomer (DPTPA) (Scheme 1) containing a TPA derivative and pyrrole. The resultant polymer was also successfully prepared. The synthesis and redox behaviors of the monomer and the polymer film are described, and the electrochemical and electrochromic properties of the polymer film are also investigated herein.

2. Experimental

All chemicals were purchased from Aldrich and used without further purification. The polymer was synthesized from a reaction medium containing 3 mM monomer and 0.1 M tetrabutylammonium perchlorate (TBAP) in boron fluoride etherate (BFEE) via constant potential electrolysis at 1.2 V versus Ag/AgCl. And the polymer was electrolyzed at 0.0 V again in order to equilibrate its redox behavior in monomer-free electrolytic solution. Indium–tin oxide (ITO) was used as working electrode, a platinum (Pt) sheet was used as counter electrode and Ag/AgCl in

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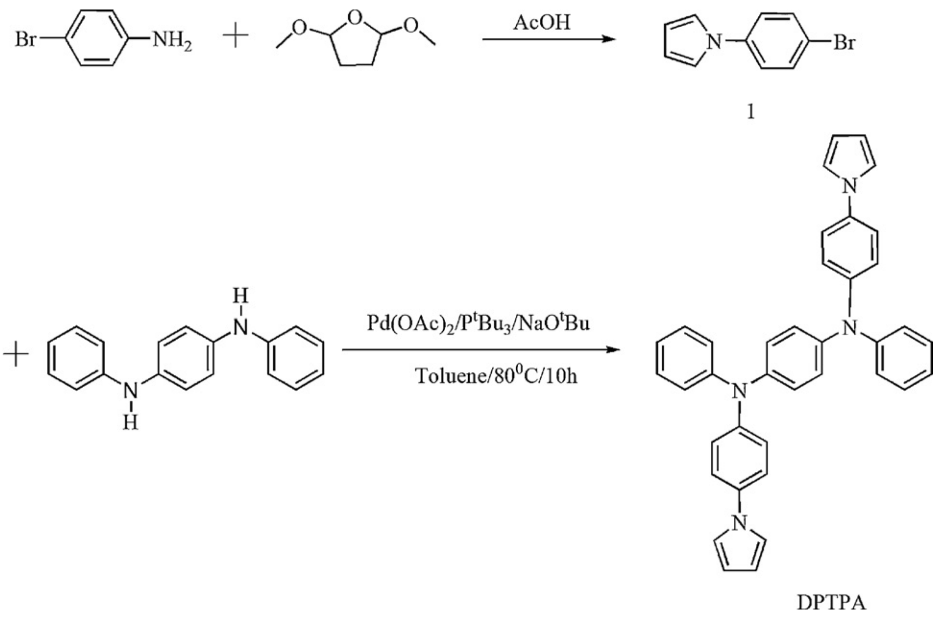

Scheme 1. Synthesis of DPTPA.

saturated KCl(aq) solution as reference. After polymerization, the films were rinsed with electrolysis solvent and transferred into another cell involving 0.1 M TBAP dissolved in BFEE solution. Electrochemical synthesis and cyclic voltammetric measurements were performed using CHI-660C electrochemical working station. An UV-1800 spectrophotometer was applied to conduct spectroelectrochemical studies. For spectroelectrochemical tests, ITO coated with the polymer film was applied as working electrode, a gyroidal Pt wire was used as counter electrode and Ag/AgCl in saturated KCl(aq) solution as reference. The transmittance and absorbance spectra of PDPTPA were recorded in situ under various applied potentials. All experiments were carried out at room temperature.

2.1. Synthesis of N^1,N^4-bis(4-(1H-pyrrol-1-yl)phenyl)-N^1,N^4-diphenylbenzene-1,4-diamine (DPTPA)

4 mM 1-(4-bromophenyl)-1H-pyrrole (1) (1 was synthesized recording to reference [22]), 2 mM N^1,N^4-diphenylbenzene-1,4-diamine and 4 mM NaO^{t}Bu were dissolved in 15 mL toluene, 0.02 g Pd(OAc)$_2$ and 2 mL PtBu$_3$ were added. The mixture was stirred in Ar atmosphere at 80 °C for 10 h. The final solution was extracted with CH$_2$Cl$_2$ and water. Then CH$_2$Cl$_2$ was removed under reduced pressure. The residue was recrystallized with ethanol for three times. The product was obtained as white powder in a 72% yield. M.P. 205 °C. ^{1}H NMR (CDCl$_3$): δ 7.30–7.27 (8H, t); 7.17–7.15 (8H, m); 7.06–7.05 (6H, t); 7.04 (4H, s); 6.35–6.34 (4H, t). ^{13}C NMR (CDCl$_3$): δ 129.3, 127.9, 125.3, 124.5, 123.8, 122.7, 121.5, 120.7, 119.4, 116.6, 110.6, 110.1. FT-IR (KBr, cm^{-1}): 3436m, 3039w, 1592m, 1517s, 1502s, 1311m, 1274s, 1118w, 1071m, 828w, 725m, 695m, 540w. MS: *m*/*z* (EI) 542 (M$^+$).

3. Results and discussion

3.1. Electropolymerization of DPTPA and electrochemical characterization

The redox behavior of DPTPA was investigated via cyclic voltammetry (CV) in 0.1 M TBAP/BFEE electrolyte solution. As seen in Fig. 1, during the first anodic scan, two reversible oxidation peaks were observed at 0.54 and 0.85 V around. During the other scans, new reversible redox couples were observed, and the current intensity of these reversible peaks increased after each successive cycle, which clearly indicated the formation of electroactive polymer film (PDPTPA) on the surface of the working electrode. The first electron removal could be assumed to occur at pyrrole group, and the second one should due to the TPA group.

DPTPA can also be electrochemically synthesized on ITO electrode in acetonitrile (ACN) solution containing 3 mM monomer and 0.1 M TBAP, and the polymer film is electrochemically stable. Two polymer films were synthesized from ACN and BFEE solution respectively. The redox behavior of the polymer film obtained from ACN solution was investigated in monomer-free 0.1 M TBAP/ACN, and the film got from BFEE solution was investigated in 0.1 M TBAP/BFEE. The CVs of the two polymer films were exhibited in Fig. 2. The two curves both displayed two couples of reversible redox peaks. The oxidation potential in BFEE was lower than that in ACN about 0.2 V. But only a very thin polymer film could be obtained in ACN solution, and the electrolyte solution around working electrode turned blue gradually in the electrolytic process. The oligomers formed afterward were dissolved or dispersed in the solution might be the reason [23].

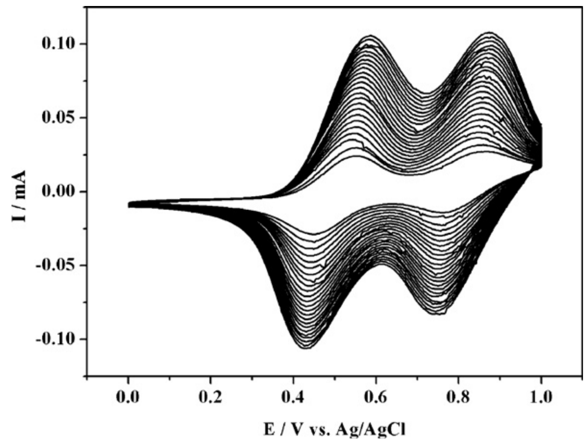

Fig. 1. Repeated cyclic voltammogram of DPTPA on ITO electrode in 0.1 M TBAP/BFEE vs Ag/AgCl at a scan rate 100 mV/s.

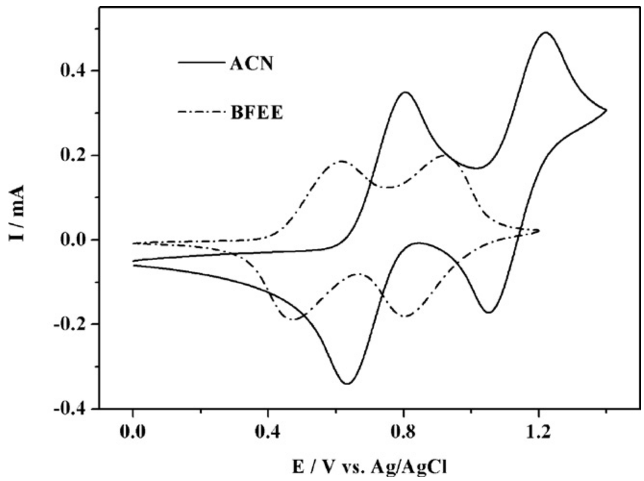

Fig. 2. CVs of PDPTPA films in monomer-free 0.1 M TBAP/ACN and 0.1 M TBAP/BFEE vs Ag/AgCl at a scan rate 100 mV/s.

Fig. 3 displayed the CV curves of PDPTPA film at different scan rates. The scan rate dependence experiments showed a linear relationship between the peak current and the scan rate, indicating non-diffusional redox process and the well-adhered electroactive polymer film [24].

3.2. FT-IR spectra

Fig. 4 exhibited the FT-IR spectra of monomer DPTPA and the resultant polymer film PDPTPA. PDPTPA film was prepared via constant potential electrolysis at 1.2 V versus Ag/AgCl, then dedoped at negative potential and washed with clean CH_2Cl_2 for three times to remove the residual supporting electrolyte and the monomers. Finally, the film was dried in vacuum at 60 °C for 10 h. As to DPTPA, the wide peak at 3436 cm^{-1} was attributed to N–H stretching in pyrrole ring, while the peaks at 1300 cm^{-1} around due to the C–N stretching. The disappearance of the peak at 3436 cm^{-1} in the spectrum of PDPTPA film demonstrates the polymerization of pyrrole group. The peak at 3039 cm^{-1} around in the spectrum of DPTPA should be ascribed to the C–H stretching in phenyl ring, the C–C stretching located at 1502 cm^{-1}, and the C–H bending of phenyl ring presented at 1071 and 725 cm^{-1}. For PDPTPA film, the degradation of peaks at 3039 and 725 cm^{-1} around implies the polymerization of TPA group.

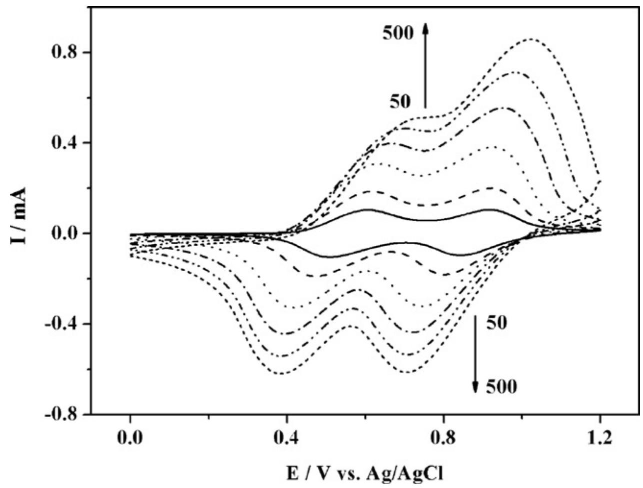

Fig. 3. Scan rate dependence of PDPTPA film on ITO electrode in 0.1 M TBAP/BFEE solution at scan rates 50, 100, 200, 300, 400 and 500 mV/s.

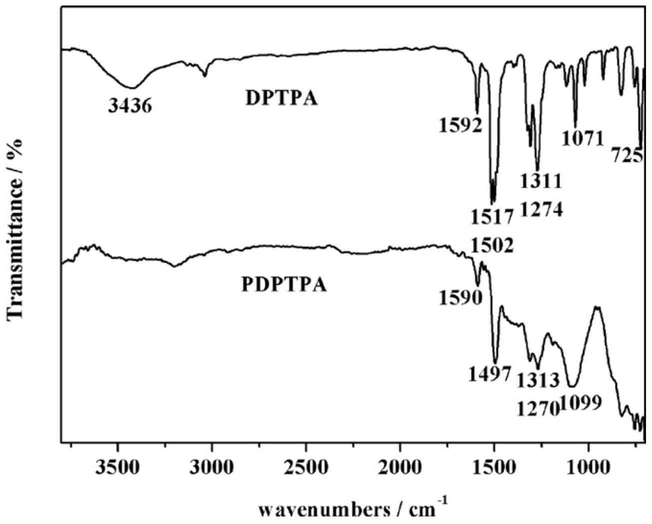

Fig. 4. FT-IR spectra of DPTPA and PDPTPA, PDPTPA film was prepared from a reaction medium containing 3 mM monomer and 0.1 M TBAP in BFEE.

3.3. Spectroelectrochemical characterization

Spectroelectrochemical analysis is a powerful way to investigate the optical switches and contrasts of EC conducting polymers upon potential change, which provides insights into the electronic structure of the conducting polymer. The spectroelectrochemical and electrochromic properties of the resultant films were studied in 0.1 M TBAP/BFEE solution.

The electrochromic absorption spectra were monitored by an UV–vis spectrometer at different applied potentials (Fig. 5). When the applied potential high up to 0.5 V, the peak at around 345 nm decreased gradually, while the peak at 410 nm around intensified and a very intense broad with a new peak at 852 nm around appeared due to the first stage oxidation. When the potential was adjusted to more positive values, it was according to the second electron oxidation [25]. The characteristic peak at 852 nm decreased, and a new band at 617 nm around appeared.

The colors of PDPTPA film at different potentials were presented in Fig. 6. From 0.0 V to 1.2 V the PDPTPA film presented six colors from brown to blue. These different colors corresponding to various doped and neutral states had also been confirmed by the CV tests, and were remained even after voltage off, indicating that the film has memory effect. Furthermore, after applying a voltage for a long time the polymer film could hold its color also. This multi-

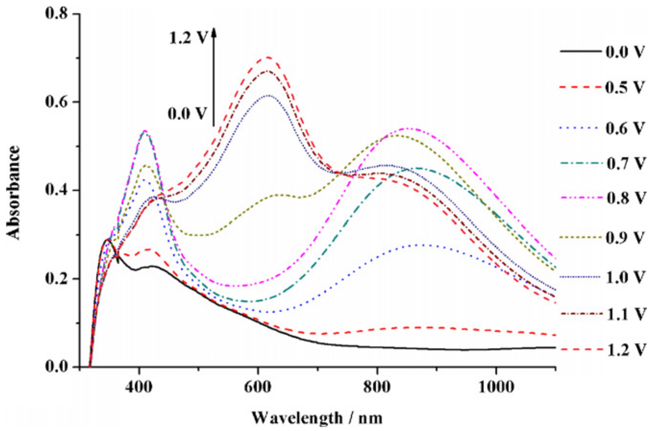

Fig. 5. Spectroelectrochemical spectra of PDPTPA film as applied potentials between 0.0 and 1.2 V in 0.1 M TBAP/BFEE.

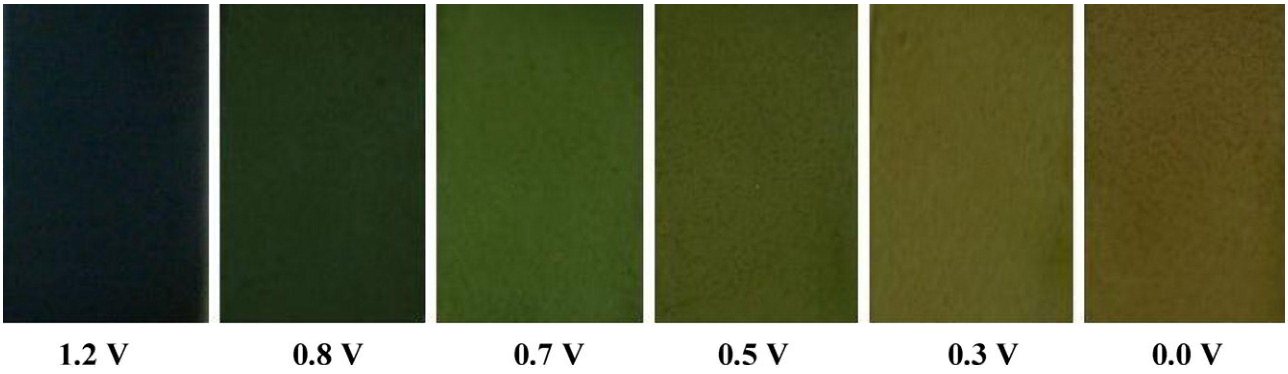

Fig. 6. Colors of PDPTPA film at different potentials.

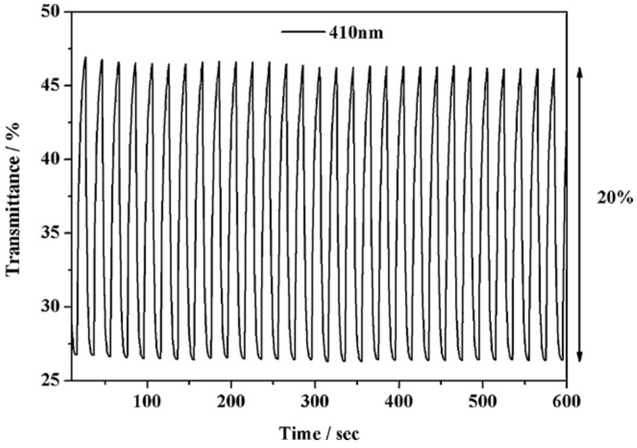

Fig. 7. Electrochromic switching, optical absorbance monitored for PDPTPA at 410 nm in 0.1 M TBAP/BFEE between 0.0 and 0.8 V with a residence time of 10 s.

color property possesses significant potential applications in smart windows or displays and so on.

3.4. Electrochromic switching

The optical switching studies of PDPTPA film were carried out in the electrolyte solution with a residence time of 10 s. At 410 and 852 nm, the film was switched between 0.0 and 0.8 V, while at 617 nm was between 0.0 and 1.2 V. The switching time was defined as the time required for reach 95% of the full change in absorbance after the switching of the potential. As seen from Figs. 7–9, the percentage transmittance changes (Δ*T*%) between the neutral and oxidized states were 20% for 410 nm, 52% for 617 nm and 41% for 852 nm. And the switching times were 1.3 s at 410 nm, 0.6 s at 617 nm and 1.4 s at 852 nm. The good stability of the Δ*T*% in time, fast switching property and high contrast ratio make this polymer a promising material for EC devices.

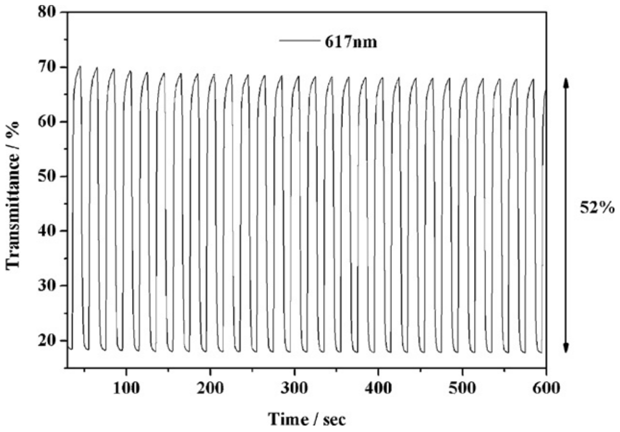

Fig. 8. Electrochromic switching, optical absorbance monitored for PDPTPA at 617 nm in 0.1 M TBAP/BFEE between 0.0 and 1.2 V with a residence time of 10 s.

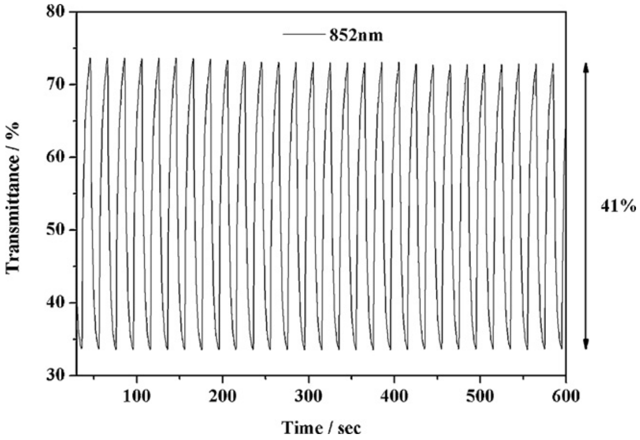

Fig. 9. Electrochromic switching, optical absorbance monitored for PDPTPA at 852 nm in 0.1 M TBAP/BFEE between 0.0 and 0.8 V with a residence time of 10 s.

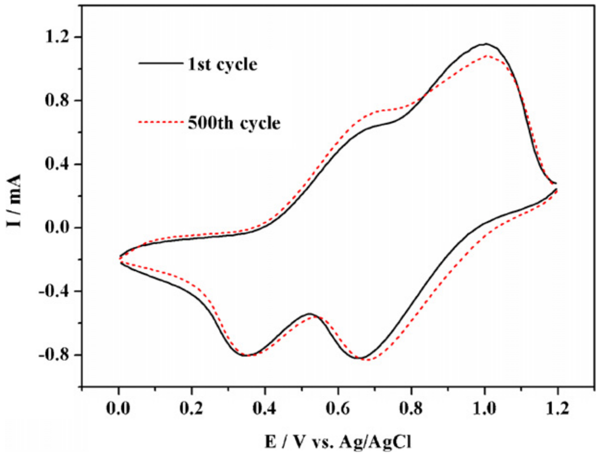

Fig. 10. CVs of PDPTPA film as a function of repeated scans 500 mV/s in 0.1 M TBAP/BFEE.

3.5. Stability of PDPTPA film

The stability of EC materials toward long-term switching between the neutral and oxidized states is one of the most important factors for the application of EC materials in device utilities. Cyclic voltammetry was used to test the stability of the polymer film. Fig. 10 presented the long-term stability of the as-prepared PDPTPA film. Cyclic voltammograms of PDPTPA film between potential 0.0 and 1.2 V indicate that the film keeps stable up to 500 cycles, only slight shrinkage of redox loop is observed after 500 cycles, which implies that PDPTPA film has reasonable stability, and could be as a promising candidate material for EC devices.

4. Conclusion

In summary, a novel multicolor polymer (PDPTPA) was electrochemically synthesized. The polymer film showed excellent multicolor electrochromism (six colors). Otherwise, the polymer film exhibited high optical contrast, fast switching time and good stability. These prominent features make PDPTPA an excellent candidate for any practical issue.

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