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Preparation and Optoelectronic Behaviours of Novel Electrochromic Devices Based on Triphenylamine-containing Ambipolar Materials

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Two new triphenylamine-containing ambipolar electrochromic materials with ether linkage, 1-(2-(4-(bis(4methoxyphenyl)amino)phenoxy)ethyl)-1'-ethyl-[4,4'-bipyridine]-1,1'-diium tetraflouroborate (TPA-Vio) and 2-(4-(bis(4methoxyphenyl)amino)phenoxy)anthracene-9,10-dione (TPA-OAQ), were synthesized successfully and fabricated into novel electrochromic devices. Such devices demonstrated interesting and much higher performance than the devices derived from the TPA-30Me such as driving voltage, switching time and electrochromic stability.

Introduction

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Basically, "chromism" refers to the colour change within the material which was subjected to an external stimulus such as light, temperature, electric field, and so on. Electrochromism can be definitely recognized as the reversible coloration in UV-vis-NIR region of materials being associated with electrochemically induced oxidative and reductive states. Generally, common electrochromic (EC) materials can be classified into four different groups including inorganic coordination complexes, transition-metal oxides, conjugated polymers, and organic molecules^{1, 2}. The electrochromic device (ECD) of active optical modules possesses lots of advantages such as high contrast, lower applied potential and power consumption, colour control and bistable characteristics. In recent years, with the increasing awareness of energy saving and carbon reduction, the EC technology is gradually drawing more attention and could be applied to smart windows for building construction, sunroof and anti-glare rear-view mirrors for vehicles, electronic papers and displays. The EC glasses have been mainly based on inorganic metal oxide for several years, but the cost of price is still becoming the brunt of major problem to produce in large quantity. Organic EC materials have gradually become promising candidate due to various characteristics, including flexibility necessary for flexible device fabrications, easy process, high coloration efficiency, and multicolour property within the same material.

Triphenylamine (TPA) derivatives are famous for their marvellous photo- and electro-active properties, and are representative alternatives for optoelectronic applications including light-emitters, hole-transporters, photovoltaic, EC and memory devices^{3, 4}. Our

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group has reported a series of electro-active high-performance polymers based on TPA derivatives in respective of synthesis and characteristic evaluation⁵. In addition, we proposed how to reduce applied oxidation potential which could enhance the electrochemical stability, and also investigated the EC colour-merging behaviours by designing different polymer structures and fabricating them into ECD construction. As contrasted with polymeric EC materials, small organic molecules have the merits such as fast mobility within the electrolyte, lower cost, and easy to tune the EC properties via facile structural modifications. According to the related studies we have published⁶, TPA could readily lose electron during electrochemical oxidation process to emerge stable radical cation with a discernible change in colour. By introducing electron-donating substituents to the p-position of phenyl groups in the TPA unit, it could not only be a protective group to prevent electrochemical oxidative coupling reaction and to afford stable cationic radicals but also decreased oxidation potential owing to their electron-donating ability, resulting in notably improved redox and EC reversibility of the obtained TPAbased materials.

Viologen derivatives are well known as organic EC materials with distinct colouring performances due to the capability of reversible optical colour change in the reduction redox cycles. By cathodic scanning, viologen would undergo reversible reduction from a dication to a monocation radical, advancing a high contrast variation in transmittance over the visible-light region⁷⁻⁹. By modifying pendent substituents of viologen structure, the colour can be tuned by means of adjusting different molecular energy levels. Moreover, anthraquinone derivatives also have drawn attention to be redoxactive and near-infrared (NIR) EC materials. Anthraquinone possesses strong electron withdrawing characteristic, and was usually used in bleaching pulp for papermaking and conjugated polymers as an electron acceptor unit.

In addition, anthraquinone derivatives are more interesting to be cathodic EC materials because of having highly electrochemical stability during reduction redox procedure¹⁰. Generally, one single EC material is not enough to achieve high contrast and full-band

Functional Polymeric Materials Laboratory, Institute of Polymer Science and Engineering, National Taiwan University, 1 Roosevelt Road, 4th Sec., Taipei 10617, Taiwan.*Email - <u>gsliou@ntu.edu.tw</u>; Fax: +886-2-33665237; Tel: +886-2-33665315 + Electronic supplementary information (ESI) available: Measurement, synthesis of 1-4, NMR spectra of 5-7 and the electrochromic data of ECD based on TPA-3OMe. See DOI: 10.1039/x0xx00000x

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absorption in visible-light region. Therefore, by collocating of anodic and cathodic EC materials together should be a judicious approach to obtain complementary in colours; moreover, it also could become mutual charge-storage layers to enhance the response capability. In the previous studies¹¹⁻¹⁴, Hsiao and our group have reported the triarylamine-based ambipolar EC polymers (e.g., polyimide, polyamide), meaning one polymer chain could exhibit interesting EC behaviours with multicolour characteristics in both oxidized and reduced states. The resulted polymers possessed some crucial properties such as excellent thermal stability, high coloration efficiency (CE), notable quick switching time (response capability), and outstanding electro-active reversibility.

In 2017, Zhou group has prepared solution type electrochromic devices derived from ambipolar materials with electron-withdrawing benzodipyrrolidone moieties¹⁵. In this article, we herein propose a facile "linkage" approach to merge ambipolar EC behaviours by using only one single small molecule. Two novel ambipolar EC materials, 1-(2-(4-(bis(4-methoxyphenyl)amino)phenoxy)ethyl)-1'-ethyl-[4,4'-bipyridine]-1,1'-diium tetrafluoroborate (6) and 2-(4-(bis(4-methoxyphenyl)amino)phenoxy)anthracene-9,10-dione (7), were

synthesized and characterized fully, then were fabricated into the EC devices to evaluate their EC performance. With the "linkage" approach, the incorporation of counter EC moieties as charge-trapping layer into TPA units can be expected to have two colours combination, reduce driving potential and switching time, and even intensify EC reversibility.

Experimental

General Considerations

TPA-3MeO was prepared by similar method in accordance with the previous literature¹⁶. Tetrabutylammonium tetrafluoroborate (TBABF₄) was given as follow procedure: DI water containing 5.00 g tetrabutylammonium bromide was dropped into saturated NaBF₄ aqueous solution. After dropwise, the solution gave desired white precipitate and then directly recrystallized from hot water. The remaining reagents were received from commercial sources and used without further purification.

Material synthesis

4-(2-Bromoethoxy)-*N*,*N*-bis(4-methoxyphenyl)aniline (TPA-OBr) (5):

A mixture of 4-(bis(4-methoxyphenyl)amino)phenol (1.4 g, 5 mmol) 4 was dissolved in 1,2-dibromoethane (20 mL, 227 mmol), then dropped potassium hydroxide solution (1.1 g, 20 mmol) with tetrabutylammonium bromide (0.026 g, 0.08 mmol) stirring at 90 °C for 24 h. After cooling to room temperature, water (100 mL) was added, and the crude product was extracted with CH_2Cl_2 then condensed and dried, giving the 1.71 g (86% in yield) of brown viscous liquid. Further purification by using flash column with eluent (dichloromethane: hexane = 1:2) to obtain the yellow liquid (78% in total yield). ¹H NMR (400 MHz, DMSO-*d6*, δ): 3.71 (s, 6H), 3.77 (t, 2H), 4.26 (t, 2H), 6.86 (m, 12H); ¹³C NMR (100 MHz, DMSO-d6, δ): 31.76, 55.53, 68.42, 115.06, 115.93, 124.38, 125.06, 141.53, 153.40, 155.11; ESI-MS m/z: calcd for ($C_{22}H_{22}BrNO_3$)⁺, 427.08 ;found, 427.09. Anal.

calcd for C₂₂H₂₂BrNO₃: C 57.74, H 4.99, N 5.94; found: ር ኤኤ. ሊዓ. ዙ 4.93, N 5.72. DOI: 10.1039/C7TC02953E

1-(2-(4-(Bis(4-methoxyphenyl)amino)phenoxy)ethyl)-1'-ethyl-[4,4'bipyridine]-1,1'-diium- tetraflouroborate (TPA-Vio) (6):

Firstly, 1.07 g (2.5 mmol) of **5** was dissolved in 60 mL acetonitrile, then 1.35 g (5.0 mmol) of 1 was added into the solution, followed by stirring at reflux temperature for 72 hours. After reaction and filtration, the filter was dissolved in DI water and added into saturated NaBF4 solution dropwisely to give precipitate. It was filtered off and dried over vacuum to obtain **6** as pale purple powder (0.920 g, 60%). M.p.: 195-200 °C measured by Melting Point System at 5 °C min⁻¹. ¹H NMR (400 MHz, DMSO-*d6*, δ): 1.60 (t, 4H), 3.70 (s, 6H), 4.52 (t, 2H), 4.71-4.76 (m, 2H), 5.13 (t, 2H), 6.84 (m, 12 H), 8.79-8.83 (m, 4H), 9.41-9.45 (m, 4H); ¹³C NMR (100 MHz, DMSO-*d6*, δ): 16.45, 55.39, 56.74, 60.34, 66.51, 114.93, 115.77, 123.91, 124.94, 126.59, 126.84, 141.22, 142.52, 145.69, 146.50, 148.71, 149.37, 152.57, 154.96; ESI-MS m/z: calcd for (C₃₄H₃₅N₃O₃)⁺, 533.27; found, 533.27. Anal. calcd for C₃₄H₃₅B₂F₈N₃O₃: C 57.74, H 4.99, N 5.94; found: C 57.79, H 4.93, N 5.72.

2-(4-(Bis(4-methoxyphenyl)amino)phenoxy)anthracene-9,10-dione (TPA-OAQ) (7):

5.53 g (40 mmol) of K₂CO₃ was firstly dissolved in 50 mL DMSO, 5.34 g (22 mmol) of 2-chloroanthraquinone and 10.55 g (20 mmol) of **4** were added into the flask successively at room temperature. The mixture was heated at 100 °C with stir for 24 hours monitored by TLC, and then slowly poured into methanol/water (1/1) after cooling. The target product was washed with hot methanol to obtain **7** as yellowish powders (9.33 g, 84%). M.p.: 144-145 °C measured by Melting Point System at 5 °C min⁻¹. ¹H NMR (400 MHz, DMSO-*d6*, δ): 3.74 (s, 6H), 6.87 (d, 2H), 6.93 (d, 4H), 7.05-7.08 (m, 6H), 7.45-7.51 (m, 2H), 7.89-7.94 (m, 2H), 8.15-8.22 (m, 3H); ¹³C NMR (100 MHz, DMSO-*d6*, δ): 55.22, 112.55, 115.01, 120.92, 121.48, 122.41, 126.53, 126.70, 127.53, 129.91, 132.98, 134.27, 134.66, 135.15, 140.14, 146.06, 147.03, 155.75, 163.11, 181.24, 182.08. ESI-MS m/z: calcd for (C₃₄H₂₅NO₅)⁺, 527.17; found, 527.18. Anal. calcd for C₃₄H₂₅NO₅: C 77.41, H 4.78, N 2.65; found: C 77.48, H 4.60, N 2.70.

Fabrication of electrochromic device

Two ITO glasses (~5 Ω/\Box) were laminated with thermosetting adhesives by full-auto dispenser and heated at 150 °C for 2 hours to obtain vacant devices with gap of 120 µm (controlled by beaded glass dispersing in the adhesives), and the active areas of devices were controlled to be 2 cm × 2 cm. Only one tiny hole was left in one side of the devices for the later injection of electrochromic liquid electrolyte. After injection of electrolyte which the total amount of propylene carbonate is ~0.048 mL inside the device based on its vacant volume, the cells were eventually sealed completely by UV gel. A liquid-type electrolyte assembly was based on **TPA-30Me** (0.015 M), **6** (0.030 M), and **7** (0.030 M), respectively, with 0.10 M TBABF₄ dissolving in propylene carbonate (PC). **Fig. 1** depicts the entire process of ECDs fabrication.

Results and discussion

Materials synthesis

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Sealed with UV-gel Liquid-type EC device Inject electrolyte by vacuum injection Yacuum injection

Fig. 1 Schematic diagram of fabrication process for ECDs based on liquid-type EC electrolyte.

TPA-30Me (m.p.: 92-93 °C by melting point system at 5 °C min⁻¹; lit.¹⁷: 90–92 °C) was obtained by copper-catalyzed reaction of *p*anisidine with 4-iodoanisole, and the result is in agreement with the previous study. **TPA-Vio (6)** was synthesized by nucleophilic substitution reaction of **5** with **1** to give yield of 60%. **TPA-OAQ (7)** was prepared by potassium carbonate-mediated reaction of **4** with 2-chloroanthraquinone to give yield of 84%. NMR spectroscopy and element analysis were used to characterize structures of the intermediate **5** and final compounds, **TPA-Vio (6)** and **TPA-OAQ (7)**. **Scheme 1** depicts the whole synthetic procedures, and the structures of the obtained intermediates and two targeted compounds (**5-7**) were confirmed well with the presented molecular structures by NMR measurements as summarized in **Fig. S1-9**, respectively.

Scheme 1 Synthesis of ambipolar TPA derivatives ${\bf 6}$ and ${\bf 7}.$



Electrochemistry

Electrochemical and EC behaviours of TPA-3OMe, 6 and 7 were investigated by cyclic voltammetry (CV) measurements using a customized OTTLE cell with 10⁻³ M of these EC materials, containing anhydrous propylene carbonate (PC) as solvent and 0.1 M of TBABF₄ as supporting electrolyte. Their CV diagrams are shown in Fig. 2, and the results of the respective half-wave redox potentials are summarized in Table 1. Comparing to TPA-**30Me**, the oxidation voltages of **6** and **7** are higher due to the replacement of one less electron-donating substituent, respectively. With the incorporation of the soft segment of ether linkage, the cathodic EC moieties within 6 and 7 could be isolated and behaved independently. Furthermore, the redox potentials of anodic (TPA) and cathodic (viologen and anthraquinone units) EC functionalities seem to be matched with each other, and could be further confirmed in the ECDs by their switching behaviours.

Spectroelectrochemistry

The spectroelectrochemical measurements were also conducted by using the same condition mentioned above using an OTTLE cell built from a commercial UV-vis cuvette to demonstrate the EC behaviours of these materials, and the results at different redox applied potentials are shown in Fig. 3.



Fig. 2 CV diagrams for 0.001 M of (a) **TPA-30Me**, (b) **6** and (c) **7** in 0.1 M TBABF₄ PC solution at the scan rate of 50 mV/s and platinum net as the working electrode.

Table 1 Redox data of TPA-3OMe, 6 and 7.

Material	Oxidation		Reduction	
	(vs. Ag/AgCl)		(vs. Ag/AgCl)	
	E _{onset} (V) ^{a)}	E _{1/2} (V) ^{b)}	E _{onset} (V) ^{a)}	E _{1/2} (V) ^{b)}
TPA-3OMe	0.53	0.61	-	-
6	0.67	0.76	-0.26	-0.35
7	0.65	0.73	-0.71	-0.84 ^{c)}

^{a)} Onset, half-wave potentials were obtained from CV.

^{b)} Half-wave potentials from cyclic voltammograms.

^{c)} Reduction potentials from cyclic voltammograms.

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Fig. 3 Electrochromic behaviour and the corresponding photographs for (a) **TPA-3OMe**, (b) **6** and (c) **7** at the applied potentials from 0 to (a) 1.0, (b) 1.0, -0.4 and (c) 1.0, -1.2 V (vs. Ag/AgCl) based on 0.001 M of material in PC containing 0.1 M of TBABF₄.

Both 6 and 7 revealed the similar results as TPA-30Me when 1.0 V was applied to the systems; 360 and 727 nm for 6 while 366 and 734 nm for 7, respectively, corresponding to the similar colour change (from transparent to cyan during oxidation procedures). For the cathodic EC behaviour, two new absorption peaks at 399 and 606 nm for 6 appeared when the potential increased from 0 to -0.4 V owing to the formation of viologen cation radicals, resulting in colour change from colourless at the original dication form to blue colour in the reduced state. For 7, the absorption of two new peaks at 402 and 543 nm could be observed and increased obviously from 0 to -1.2 V. The formation of monoanion radical in the anthraquinone moiety switches the colour from almost colourless to pink. Furthermore, in order to get more insight to the EC behaviours of the ambipolar materials, two slices of ITO coated glass were used as working and auxiliary electrodes, respectively, to simulate the coloration mechanism in the device system. By using 6 as example, it exhibited reversibly colouring and bleaching changes on both electrodes in the same time at the applied potential of 0.8 V as depicted and proposed in the Fig. 4.



Fig. 4 The schematic diagram of colour change for the ambipolar materials using **6** as model with quartz glass square at the applied potential 0.8 V (vs. Ag/AgCl).



Fig. 5 CV diagrams of ECDs containing 0.03 M of (a) **6** and (b) **7** in 0.1 M of TBABF₄/PC solution at the scan rate of 50 mV/s. One of the ITO glass served as the working electrode and the other ITO glass simultaneously served as counter electrode and reference electrode.

Electrochromic devices and properties

Moreover, ECDs derived from ambipolar EC materials **6** or **7** revealed the same redox driving voltage, respectively, to achieve coloured stage regardless of the different phases of applied voltage (**Fig. 5a**), and the working potential for **6** (1.2 V) was much lower than the device derived from **TPA-3OMe** (2.2 V; **Fig. S10**). In addition, the incorporation of counter EC moieties not only have the effect to reduce the driving voltage, the absorption of new peaks in visible-light region at 606 nm (viologen unit) and 724 nm (TPA unit) for **6** gradually increased simultaneously and could be merged together to reach high Δ T% of 87% at 606 nm and 96% at 724 nm as shown in **Fig. 6a** and **b**.



Fig. 6 (a) Absorbance spectrum and (b) transmittance spectrum of ECD based on **6** at the applied potential from 0 to 1.2 V and its corresponding photograph. (c) Absorbance spectrum and (d) transmittance spectrum of ECD based on **7** at the applied potential from 0 to 1.8 V and its corresponding photograph.

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Thus, two complementary colours (cyan and blue) could be merged together, resulting in much deeper blue colour and higher ΔL^* (L*, 91.38-40.09; a*, 0.25-13.09; b*, 0.28-52.54).

Similarly, the absorption intensity at 535 nm (anthraguinone unit) and 734 nm (TPA unit) could also increase simultaneously at higher applied voltage of 1.8 V for the other device based on ambipolar material 7, and could combine two complementary colours (cyan and pink) with Δ T% of 68% at 535 nm and 91% at 734 nm to produce a deeper violet colour (L*, 68.51; a*, 2.50; b*, -11.36) of the device as shown in Fig. 6c and d. As the potential voltage turned off to 0 V, both of the devices could easily bleach back to their original states. This outcome could be partly responsible for the viologen/anthraquinone moieties possessing the capability to induce the electrons losing from TPA moiety during oxidative process, and then the resulted monocation radical viologen and monoanion radical anthraquinone also could facilitate electrons back to monocation TPA during reductive process.

According to the switching investigation of ECDs based on the individual ambipolar EC materials, the results are summarized in **Fig. 7**. As depicted in **Fig. 7a** and **b**, the switching time of ECD derived from **6** exhibited 1.7 s and 2.7 s at 1.2 V for coloring process at 724 nm (TPA moiety) and 606 nm (viologen moiety), while 9.7 s and 9.5 s, respectively, for bleaching process without applied voltage.



Fig. 7 Transmittance changes at (a) 724 nm and (b) 606 nm, and (c) chronoamperometry curve of device containing **6** between 0 and 1.2 V. Transmittance changes at (d) 535 nm and (e) 734 nm, and (f) chronoamperometry curve of device containing **7** between 0 and 1.8 V.



Fig. 8 Chronoamperometry curves and the corresponding in situ absorbance at the respective wavelengths of ECDs with (a) 6 between 0 and 1.2 V; (b) 7 between 0 and 1.8 V.

The other device based on 7 as shown in Fig. 6d and e required 5.5 s for coloration at 535 nm and 5.3 s for decolouration (anthraquinone moiety); 3.2 s for coloration at 734 nm at 1.8 V and 5.2 s for decolouration (TPA moiety) without applied voltage.

The results summarized in **Table S1** are noteworthy that the colouration of ECDs with ambipolar materials proceeded during the colouring process faster than the corresponding ECD based on **TPA-30Me** EC material only with anodic EC unit owing to the fact that the connecting charge trapping moieties in the **6** and **7** could effectively induce the electron gaining and losing. The amount of injected charge (Q_{in}) obtained from **Fig. 7c** and **f** were 14.012 and 14.134 mC/cm² for colouring process of devices with **6** and **7**, respectively. According to the results described above, such devices demonstrated enhanced performance comparing to the device with **TPA-30Me** (**Fig. S11a**).

As shown in Fig. 8, the electrochemical stability of the ECDs based on 6 and 7 was determined by evaluating the electrochromic CE ($\eta = \Delta OD/Q$) and injected charge (electroactivity) at various switching cycles, and the results are summarized in Table S2 and S3, respectively. After 1000 scanning cycles, both ECDs derived from 6 and 7 ambipolar EC materials still could maintain high reversibility and electroactivity without significant decay, while the ECD derived from TPA-30Me exhibited much worse electrochemical stability even only for 20 cycles (Fig. S11c), probably owing to the much higher switching potential and without complementary cathodic EC moieties. The CE of ECD fabricated from 6 could reach to 112 and 177 cm²/C at 606 and 724 nm, and remain their reversibility with decay of 7 and 6%, respectively, after 1000 cycles between 0 and 1.2 V. On the other hand, the CE of ECD prepared from 7 showed CE 72 and 162 cm²/C at 535 and 734 nm, respectively, with decay of 10 and 5% after 1000 cycles. These outcomes are also in agreement with the assumption mentioned above that the incorporation of counter EC moieties into TPA unit could effectively improve the switching response time and enhance the electrochemical stability.

Conclusions

The high-performance ECDs with ambipolar EC materials **TPA-Vio (6)** and **TPA-OAQ (7)** have been fabricated successfully and investigated on the basis of spectroelectrochemical and EC switching studies, respectively. By the incorporation of cathodic

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EC moieties into TPA as charge trapping layer, the resulted ambipolar ECDs not only could reduce the driving voltage and switching time over the EC procedure when compared to the devices only with TPA, but also reveal the capability to merge the colours contributed from both anodic TPA and cathodic EC moieties. Therefore, the electrochemical stability and EC performance of the obtained ECDs containing ambipolar EC materials could be further enhanced than ever. These results demonstrate and manifest conclusively that the incorporation of suitable counter EC moieties into TPA derivatives should be a facile and feasible approach to fabricate novel ECDs.

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By combining anodic and cathodic moieties into an ambipolar material via the ether linkage, the electrochromic performance could be enhanced.

