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A novel panchromatic shutter based on an ambipolar electrochromic system without supporting electrolyte†

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Two triphenylamine derivatives, *N,N,N',N'*-tetrakis(4-methoxyphenyl)-1,4-phenylenediamine TPPA and *N,N,N',N'*-tetrakis(4-methoxyphenyl)-1,1'-biphenyl-4,4'-diamine TPB, were successfully prepared and combined with HV to fabricate the electrochromic device as a panchromatic shutter for the application of transparent display. The obtained electrochromic device exhibits exceptional novel electrochromic properties, including enhanced color contrast, switching time, and long-term stability. Furthermore, it is worth mentioning that the most important contribution of this ambipolar system approach is that no supporting electrolyte is added into the device.

Fundamentally, aromatic amines (arylamines) are colourless at the neutral state, and could be used as promising electrochromic materials by virtue of their plentiful EC behaviour when a form of radical-cation is generated, caused by mono-electron oxidation. The nitrogen centre of triphenylamine (TPA), which is rich in electron density, can be easily oxidized to give a stable radical-cation form accompanied by an outstanding colour change. Consequently, research about the synthesis and electrochromic (EC) properties of polymers incorporated with triarylamine units has been reported in various publications.^{1–7} Since 2002, our group has successfully synthesized TPA-based polymers with not only excellent film-forming capability by solution casting but also high transparency and thermal stability due to the propeller-like TPA moieties, which are bulky and non-coplanar. These solution-processable high-performance polymers with TPA units could be used as remarkable electrochemical working positions. As an EC functional moiety, the TPA unit has two basic properties: one is its easily oxidized nitrogen centre and the other is its hole-transporting ability *via* the species at the radical cation state. The behaviour of TPA oxidation has been well studied in preceding publications.^{8–15} To serve as a transcendent shutter of

an electrochromic device (ECD), the contrast of the transmittance over the whole visible light region, switching time, and long-term electrochemical stability are the most critical and crucial issues for practical application. Several research papers have been published in the past few years which all report a colourless, transmissive ECD at the neutral state.^{16–18} In particular, in 2017, a highly transparent to truly black panchromatic ECD based on TPA-based polyamides has been successfully fabricated and reported by our group.¹⁹ Although the optical transmittance contrast of the ECD was high ($\Delta T\% = 60\%$), the response capability in terms of the time needed for the switching and bleaching process is still not quick enough, which may hamper the applicability. To overcome this crucial disadvantage without sacrificing any of the other excellent EC characteristics, it is necessary to modify both the EC materials and device's fabrication technique to obtain a novel ECD shutter.

In this study, *N,N,N',N'*-tetrakis(4-methoxyphenyl)-1,4-phenylenediamine (TPPA) and *N,N,N',N'*-tetrakis(4-methoxyphenyl)-1,1'-biphenyl-4,4'-diamine (TPB), as shown in Fig. 1a, were readily prepared for a liquid type ECD, for which the fabrication is depicted in Fig. 1b.²⁰ The resulting devices, with the combination of heptyl viologen (HV) to give TPPA/HV and TPB/HV, demonstrated excellent EC performance as shown in Fig. S1–S4 (ESI†). Hence, these three EC materials were further merged into one device as a novel panchromatic shutter.

TPPA and TPB were synthesized *via* the Buchwald–Hartwig amination following the previous literature, with a yield higher than 80%, as shown in Scheme 1, and their ¹H NMR spectra demonstrated good agreement with the proposed structure, as shown in Fig. S5–S7 (ESI†).^{21,22}

The electrochemical behaviour was investigated by carrying out cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements as shown in Fig. 2a and Fig. S8 (ESI†), respectively. The spectroelectrochemical measurements were then used to investigate the EC behaviour, as shown in Fig. 2b and c. According to Fig. 2b, the characteristic peaks for TPPA (413 nm), TPB (511 nm) and HV (606 nm) increased obviously at the applied potential of 1.2 V. When the applied potential is

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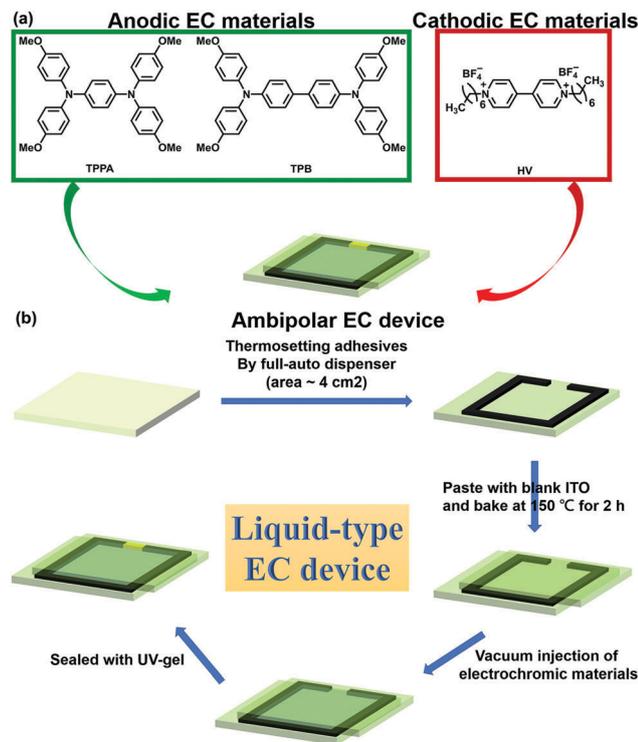
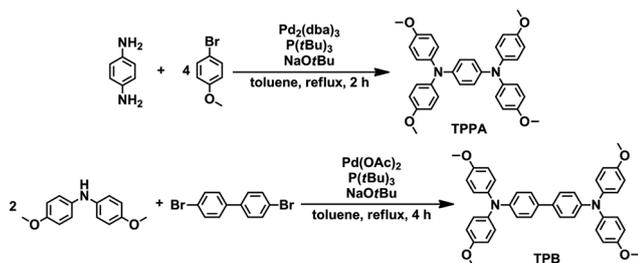


Fig. 1 (a) Schematic of the ambipolar ECD and EC materials. (b) Schematic of the procedures for the liquid-type ECD.



Scheme 1 Synthesis routes of TPPA and TPB.

higher than 1.2 V, the system will proceed to the second oxidation state. Consequently, 1.2 V was chosen as the working potential to conduct further experiments. The resulting transmittance spectra, using air as the background, revealed an extremely high average optical transmittance contrast ($\Delta T\%$ up to 70%) over the visible light region (425–675 nm) between the bleaching (off) and switching (on) states at the applied potentials 0 and 1.2 V, respectively, as depicted in Fig. 2c. The CIE chromaticity calculated from the transmittance spectra of the ECD, using air as the background, is presented in Fig. 2d. The ECD exhibited high L^* (91.60) and low colour opponent dimensions ($a^* = -5.85$ and $b^* = 4.50$) at 0 V indicating high transparency and colourlessness at the neutral off state. Meanwhile, the ECD changed to low L^* (17.94) with low colour opponent dimensions ($a^* = 0.34$ and $b^* = 0.60$), implying a truly black appearance at the on-state (1.2 V).

Afterwards, an interesting experiment, that of removing the supporting electrolyte, was carried out to prove that HV could

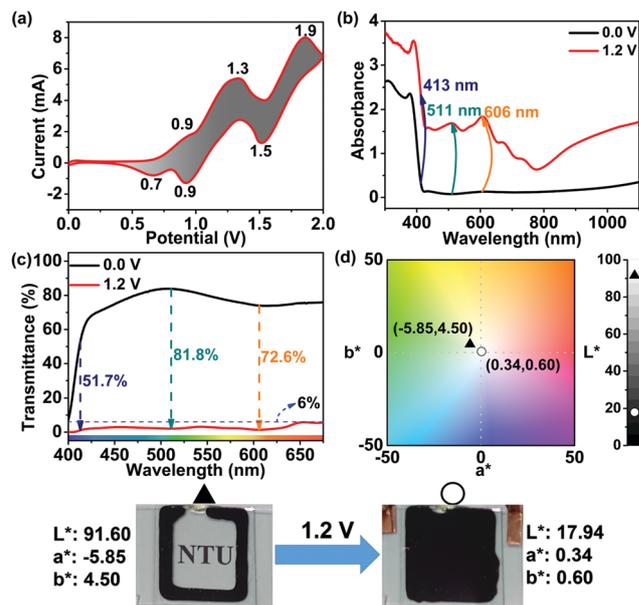


Fig. 2 (a) CV diagram for the ECD derived from TPPA/TPB/HV at the scan rate of 50 mV s⁻¹. (b) Absorbance spectra, (c) corresponding transmittance spectra, using air as the background, at the applied potentials of 0.0 V and 1.2 V and (d) CIE chromaticity diagram for the TPPA/TPB/HV based ECD. The device is derived from ITO glass with a 2 cm × 2 cm active area, containing 0.01 M TPPA, 0.03 M TPB and 0.04 M HV in 0.05 mL PC/GBL (1/1) co-solvent with 0.16 M TBABF₄ as the supporting electrolyte.

not only serve as the cathodic EC material but also play the role of the supporting electrolyte in the ECD of an ambipolar system. According to the CV result displayed in Fig. 3a, the difference in applied potential between the second and third oxidation stages for the modified one is larger and obvious compared to the original one with TBABF₄ as the supporting electrolyte shown in Fig. 2a, implying that TPPA and TPB in the modified device could be maintained at their first oxidation stage more precisely when the applied potential is set at 1.2 V. In addition, the results of spectroelectrochemical measurement also display the absorbance and transmittance difference between the original and modified ECD depicted in Fig. 3b and c, respectively. An unexpected result revealed that the absorbance intensity for the latter one was higher than that for the original one with TBABF₄ as the supporting electrolyte, and the average transmittance over the visible light region attained only 1% at the on-state, as shown in Fig. 3b and c and Fig. S9 (ESI[†]), respectively. According to the CIE chromaticity displayed in Fig. 3d, the modified ECD exhibited almost the same results (L^* , a^* and b^* values) and optical transparency as the original one at the off-state, indicating that the ECDs have high transparency ($L^* = 91.79$) and low colour opponent dimensions ($a^* = -6.02$ and $b^* = 5.13$). Meanwhile, the modified ECD had a much lower lightness ($L^* = 5.50$) and values of colourless opponent dimensions ($a^* = 0.87$ and $b^* = -0.03$) at the on-state, meaning that the modified device has extremely high optical contrast ($\Delta L^* = 86$), which is much higher than that of the original one ($\Delta L^* = 74$).

The EC characteristics (switching time and coloration efficiency) in the switching procedure carried out between 1.2 V

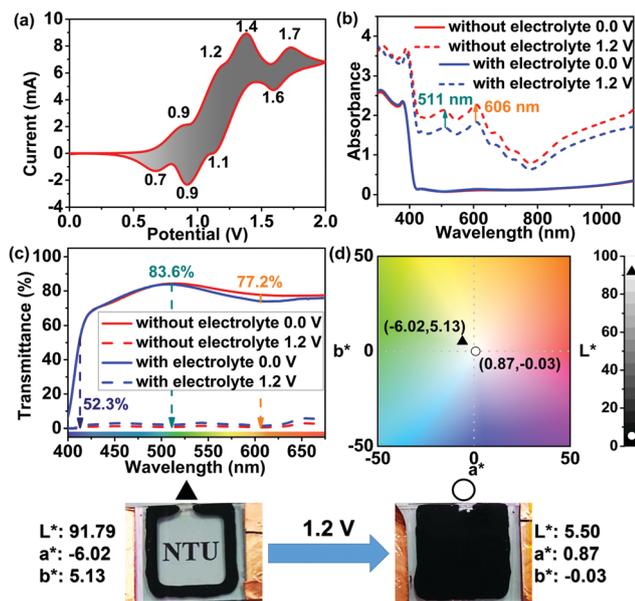


Fig. 3 (a) CV diagram for the ECD derived from TPPA/TPB/HV at the scan rate of 50 mV s^{-1} . Comparison of (b) absorbance spectra and (c) corresponding transmittance spectra between these two devices with and without supporting electrolyte, using air as the background, at the applied potentials of 0.0 V and 1.2 V. (d) CIE chromaticity diagram for the TPPA/TPB/HV based ECD. The device is derived from ITO glass with a $2 \text{ cm} \times 2 \text{ cm}$ active area, containing 0.01 M TPPA, 0.03 M TPB and 0.04 M HV in 0.05 mL PC/GBL (1/1) co-solvent without supporting electrolyte.

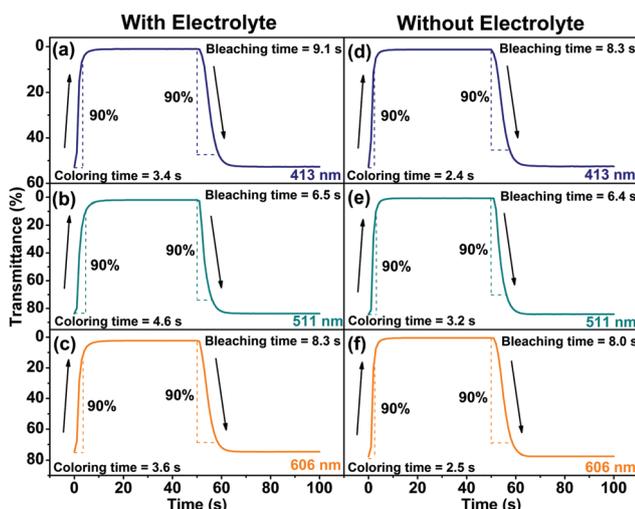


Fig. 4 (a–c) EC switching response test at each specific wavelength between 1.2 V (on-state) and -0.1 V (off-state) for the TPPA/TPB/HV based ECD, which is same as the one in Fig. 2. (d–f) EC switching response test at each specific wavelength between 1.2 V (on-state) and -0.1 V (off-state) for the TPPA/TPB/HV based ECD, which is same as the one in Fig. 3.

(on) and -0.1 V (off) are summarized in Fig. 4 and Fig. S10 and S11 (ESI[†]). Fig. 4a–c demonstrate the switching response times for the ECD at each specific characteristic wavelength shown in Fig. 2b, ranging from 4.6 s for 511 nm (main peak for TPB^{•+}) to 3.3 s for 413 nm (main peak for TPPA^{•+}), with an average colouring time of about 4 s while the average bleaching time is about 8 s,

ranging from 9.1 s for 413 nm to 6.5 s for 511 nm, which could be attributed to the low bleaching voltage. In addition, the coloration efficiency (CE) was calculated from Fig. 4a–c and Fig. S10a (ESI[†]). According to previous literature,²³ the CE for the ECD should be the sum of all CEs for each material used in the ECD, thus our device could have a CE of up to $1000 \text{ cm}^2 \text{ C}^{-1}$, as shown in Fig. S10b (ESI[†]). Compared to the results reported recently by our group shown in Fig. S10c and d (ESI[†]), and literature published by Naomi J. Halas *et al.*, our device exhibits a better result.^{20,24} Furthermore, the switching behaviour of the modified ECD (without TBABF₄) was also investigated and the results are summarized in Fig. 4d–f. After removing the supporting electrolyte, the response time for the colouring process at all the characteristic absorption peaks displayed an average time of about 3 s, which is 1 s faster than that of the original one with supporting electrolyte. Nevertheless, the average response time for the bleaching process time showed only a little enhancement of about 0.4 s, and the overall coloration efficiency (CE) revealed no obvious difference between these two devices, as shown in Fig. S11 (ESI[†]).

Finally, the long-term EC stability of the modified ECD was tested and the results are depicted in Fig. 5. In the first cycle, the device showed high stability at the on-state, with the decay in optical transmittance being less than 1% after 8 hours, and further cycles still revealed exceeding EC stability (total 32 hours). Turning our attention to the off-state, the device

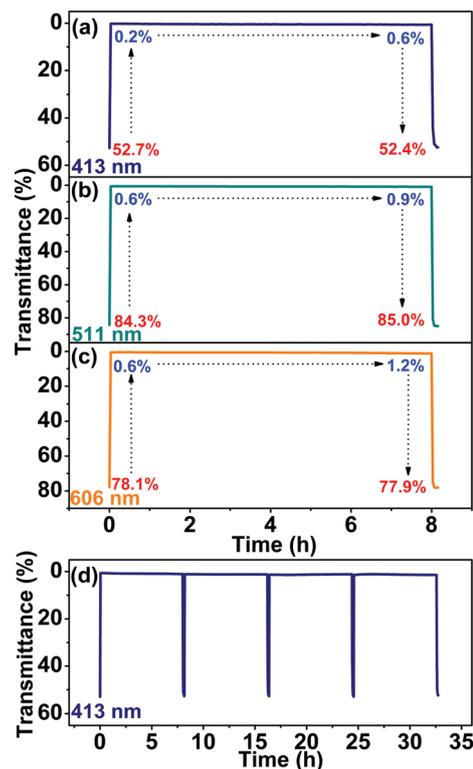


Fig. 5 Electrochromic long-term stability of (a–c) one switching cycle at the corresponding wavelength and (d) four switching cycles at 413 nm for the modified ECD based on TPPA/TPB/HV between 1.2 V (on-state) for 8 hours and -0.1 V (off-state) for 10 minutes. The device is the same as the one in Fig. 3.

could also fully return to the original transparent state not only in the first cycle but also in the rest of the cycles.

In conclusion, two kinds of high-performance ECD, with and without supporting electrolyte, derived from the ambipolar materials **TPPA**, **TPB** and **HV**, were fabricated successfully. Unexpectedly, **HV** not only could serve as the cathodic EC material but also as the supporting electrolyte. This concept is facile but novel for future application in this research area. The removal of the supporting electrolyte did not make the device fail to operate but enhanced the performance of the device in terms of the optical transmittance contrast (ΔL^* : 74 \rightarrow 86), giving the highest result to the best of our knowledge. Besides, the EC switching response time (average colouring time: 3.9 s \rightarrow 2.7 s) was also much faster compared to that in our previous report.¹⁹ Furthermore, the modified device revealed excellent long-term EC stability without obvious decay for more than 32 hours continuously. Consequently, this novel ambipolar ECD with low driving voltage, exceedingly high optical contrast over the visible light region, quick switching time and without the addition of any supporting electrolyte could be claimed to be a truly “transparent-to-black” ECD, implying high potential for the application as a panchromatic shutter for transparent displays.

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Conflicts of interest

There are no conflicts to declare.

References

1 Y. Oishi, M. Ishida, M. A. Kakimoto, Y. Imai and T. Kurosaki, *J. Polym. Sci., Part A: Polym. Chem.*, 1992, **30**, 1027.

- 2 K. Ogino, A. Kanegae, R. Yamaguchi, H. Sato and J. Kurjata, *Macromol. Rapid Commun.*, 1999, **20**, 103.
- 3 W. L. Yu, J. Pei, W. Huang and A. J. Heeger, *Chem. Commun.*, 2000, 681.
- 4 G. S. Liou, S. H. Hsiao, M. Ishida, M. Kakimoto and Y. Imai, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**, 3815.
- 5 G. S. Liou and S. H. Hsiao, *J. Polym. Sci., Part A: Polym. Chem.*, 2003, **41**, 94.
- 6 M. K. Leung, M. Y. Chou, Y. O. Su, C. L. Chiang, H. L. Chen, C. F. Yang, C. C. Yang, C. C. Lin and H. T. Chen, *Org. Lett.*, 2003, **5**, 839.
- 7 S. H. Hsiao, C. W. Chen and G. S. Liou, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 3302.
- 8 S. H. Cheng, S. H. Hsiao, T. H. Su and G. S. Liou, *Macromolecules*, 2005, **38**, 307.
- 9 H. J. Yen and G. S. Liou, *Chem. Mater.*, 2009, **21**, 4062.
- 10 H. J. Yen, H. Y. Lin and G. S. Liou, *Chem. Mater.*, 2011, **23**, 1874.
- 11 H. J. Yen, K. Y. Lin and G. S. Liou, *J. Mater. Chem.*, 2011, **21**, 6230.
- 12 H. J. Yen, C. J. Chen and G. S. Liou, *Adv. Funct. Mater.*, 2013, **23**, 5307.
- 13 J. H. Wu and G. S. Liou, *Adv. Funct. Mater.*, 2014, **24**, 6422.
- 14 D. Weng, Y. C. Shi, J. M. Zheng and C. Y. Xu, *Org. Electron.*, 2016, **34**, 139.
- 15 H. J. Yen, C. L. Tsai, S. H. Chen and G. S. Liou, *Macromol. Rapid Commun.*, 2017, **38**, 1600715.
- 16 D. Gulfidan, E. Sefer, S. Koyuncu and M. H. Acar, *Polymer*, 2014, **55**, 5998.
- 17 G. Tahtali, Z. Has, C. Doyranli, C. Varlikli and S. Koyuncu, *J. Mater. Chem. C*, 2016, **4**, 10090.
- 18 D. Weng, Y. C. Shi, J. M. Zheng and C. Y. Xu, *Org. Electron.*, 2016, **34**, 139.
- 19 H. S. Liu, B. C. Pan, D. C. Huang, Y. R. Kung, C. M. Leu and G. S. Liou, *NPG Asia Mater.*, 2017, **9**, e388.
- 20 D. C. Huang, J. T. Wu, Y. Z. Fan and G. S. Liou, *J. Mater. Chem. C*, 2017, **5**, 9370.
- 21 B. A. Kamino, B. Mills, C. Reali, M. J. Gretton, M. A. Brook and T. P. Bender, *J. Org. Chem.*, 2012, **77**, 1663.
- 22 L. L. Hill, L. R. Moore, R. C. Huang, R. Craciun, A. J. Vincent, D. A. Dixon, J. Chou, C. J. Woltermann and K. H. Shaughnessy, *J. Org. Chem.*, 2006, **71**, 5117.
- 23 L. C. Chen and K. C. Ho, *Electrochim. Acta*, 2001, **46**, 2151.
- 24 G. J. Stec, A. Lauchner, Y. Cui, P. Nordlander and N. J. Halas, *ACS Nano*, 2017, **11**, 3254.