View Article Online View Journal

ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: J. Wu and G. Liou, *Chem. Commun.*, 2018, DOI: 10.1039/C8CC00224J.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/chemcomm



Journal Name

COMMUNICATION

Novel Panchromatic Shutter Based on Ambipolar Electrochromic System without Supporting Electrolyte

Received 00th January 20xx, Accepted 00th January 20xx

Jung-Tsu Wu and Guey-Sheng Liou*

DOI: 10.1039/x0xx00000x

www.rsc.org/

Two triphenylamine derivatives, N,N,N',N'-tetrakis(4methoxyphenyl)-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 panchromatic shutter for the application of transparent display. The obtained electrochromic device exhibits exceptional novel electrochromic properties, including enhanced coloring contrast, switching time, and long-term stability. Furthermore, the most important contribution by this ambipolar system approach is without adding supporting electrolyte into the device that is worth mentioning.

Basically, aromatic amines (arylamines) are colourless at neutral state, and could be used as promising electrochromic materials in virtue of their plentiful EC behaviours when a form of radical-cation shows up caused by the mono-electron oxidation. The nitrogen centre of triphenylamine (TPA) which is rich in electron can be easily oxidized to give birth to a stable radical-cation form accompanied with an outstanding colour change. Consequently, researches about synthesis and electrochromic (EC) properties of polymer incorporated with the triarylamine units have been issued in the publications.¹⁻⁷ Since 2002, our group has successfully synthesized TPA-based polymers with not only excellent film-forming capability by solution casting but exhibiting high transparency and thermal stability due to the propeller-liked TPA moieties which are bulky and non-coplanar. These solution-processable highperformance polymers with TPA units could be used as remarkable electrochemical working positions. As an EC functional moiety, the TPA unit brings out two basic properties, one is its easily oxidized nitrogen centre and the other is holetransporting ability via the species at radical cation state. The behaviour for TPA oxidation have been well studied in the preceding publications.⁸⁻¹⁵ To serve as a transcendent shutter of 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 the practical application. Several researches have been published in the past few years which all display a colourless, transmissive ECD at the neutral state.¹⁶⁻¹⁸ Especially in 2017, a highly transparent to truly black panchromatic ECD based on TPA-based polyamides has been successfully fabricated and reported in our group.¹⁹ Although the optical transmittance contrast of the ECD was high (Δ T% = 60%), but the response capability in terms of the time needed for switching and bleaching process is still not quick enough



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

^{a.} Institute of Polymer Science and Engineering, National Taiwan University, 10607, Taipei, Taiwan

E-mail: gsliou@ntu.edu.tw.

Electronic Supplementary Information (ESI) available: [Experiment section, electrochromic properties of **TPPA/HV** and **TPB/HV**, 1^H NMR spectra, coloration efficiency, display video]. See DOI: 10.1039/x0xx00000x

Published on 12 February 2018. Downloaded by University of Windsor on 19/02/2018 17:33:43.

Scheme 1 Synthesis routes of TPPA and TPB



which may hamper the applicability. To overcome this crucial disadvantage without scarifying any other excellent EC characteristics, both the EC materials and device's fabricating technique are necessary to be modified for obtaining novel ECD shutter.

In this study, N,N,N',N'-tetrakis(4-methoxyphenyl)-1,4phenylenediamine (**TPPA**) and N,N,N',N'-tetrakis(4methoxyphenyl)-1,1'-biphenyl-4,4'-diamine (**TPB**) as shown in Fig. 1a were readily prepared for liquid type ECD which the fabrication is depicted in Fig. 1b.²⁰ The resulted devices with the combination of heptyl viologen (**HV**) as **TPPA/HV** and **TPB/HV** demonstrated excellent EC performance as shown in Fig. S1-4 (Supporting Information). 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 literatures with a yield higher than 80% as shown in Scheme 1 and their 1^H NMR spectra demonstrated good agreement to the proposed structure as shown in Fig. S5-7 (Supporting Information).^{21, 22}

The electrochemical behaviours were carried out by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements as shown in Fig. 2a and Fig. S8 (Supporting



Fig. 2 (a) CV diagram for the ECD derived from TPPA/TPB/HV at the scan rate of 50 mV/s. (b) absorbance spectra, (c) corresponding transmittance spectra using air as background at the applied potential of 0.0 V and 1.2 V and (d) CIE chromaticity diagram for the TPPA/TPB/HV based ECD. Device is derived from ITO glass with 2 cm × 2 cm

active area, containing 0.01 M of TPPA, 0.03 M of TPB and 0.04 M of HV in 0.05 mL PC/GBL (1/1) co-solvent with 0.16 M of TBABF₄ as the supporting electrolyte.

Information), respectively. The spectroelectrochemical measurement was 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 (511nm) and HV (606 nm) increased obviously at the applied potential of 1.2 V. When the applied potential is 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 resulted transmittance spectra using air as background revealed extremely high average optical transmittance contrast (Δ T% up to 70%) over the visible light region (425-675 nm) between the bleaching (off) and switching (on) states at the applied potential 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 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 colourless at the neutral off state. While, 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 on-state (1.2 V).

Afterwards, an interesting attempt, removing the supporting electrolyte, was applied to prove that the HV could not only serve as the cathodic EC material but also play the role of supporting electrolyte in the ECD of ambipolar system. According to the CV result displayed in Fig. 3a, the difference of applied potential between the second and third oxidation stages for the modified one is larger and obvious comparing to the original one with TBABF₄ as the supporting electrolyte shown in Fig. 2a,



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

DOI: 10.1039/C8CC00224J

Journal Name

Published on 12 February 2018. Downloaded by University of Windsor on 19/02/2018 17:33:43.



Fig. 4 (a-c) EC switching response test at each specific wavelength between 1.2 V (onstate) 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.

implying that TPPA and TPB in the modified device could maintain at their first oxidation stage more precisely when applied potential is set at 1.2 V. In addition, the results of spectroelectrochemical measurement also displayed 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 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, c and S9 (Supporting Information), 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 the ECDs have high transparency (L^* = 91.79) and low colour opponent dimensions (a* = -6.02 and b* = 5.13), respectively. While, the modified ECD manifested a much lower lightness ($L^* = 5.50$) and the values of colourless opponent dimensions (a* = 0.87 and b* = -0.03) at on-state, meaning the modified device has extremely high optical contrast ($\Delta L^* = 86$) which is much higher than the original one $(\Delta L^* = 74).$

The EC characteristics (switching time and coloration efficiency) in the switching procedure carried out between 1.2 V (on) and -0.1 V (off) are summarized in Fig. 4 and Fig. S10, 11 (Supporting Information). Fig. 4a-c demonstrate the switching response times for ECD at each specific characteristic wavelength signed 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 average colouring time 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 (Supporting Information). According to the previous literature,²³ the CE for the ECD should be the sum of all CE for each material used in the ECD, thus our device could be up to 1000 cm^2/C as shown in Fig. S10b (Supporting Information). Comparing to the results

reported recently in our group shown in Fig. S10c, S10d, 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



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. Device is same as Fig. 3.

results are summarized in Fig. 4d-4f. After removing the supporting electrolyte, the response time for colouring process at all the characteristic absorption peaks displayed an average time about 3 s which is 1 s faster than the original one with supporting electrolyte. Nevertheless, the average response time for the bleaching process time showed only little enhancement about 0.4 s, and the overall coloration efficiency (CE) revealed no obvious difference between these two devices as shown in Fig. S11 (Supporting Information).

Finally, the long-term EC stability of the modified ECD was conducted 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 less than 1% after 8 hours, and the further cycles still revealed exceeding EC stability (total 32 hours). Turning our glare to the off-state, the device also could fully return to the original transparent state not only in the first cycle but the rest cycles.

In the conclusion, two kinds of high-performance ECDs, with and without supporting electrolyte, derived from ambipolar materials of **TPPA**, **TPB** and **HV** were fabricated successfully. Unexpectedly, **HV** not only could serve as the cathodic EC material but also the supporting electrolyte, the concept is facile but novel for the future application in this research area. The removal of the supporting electrolyte did not make the device fall out of operation but enhanced the performance of

COMMUNICATION

the device in optical transmittance contrast (Δ L*: 74 \rightarrow 86) which is 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) also displayed much faster when compares to 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 adding any supporting electrolyte could be claimed to serve as a truly "transparent-to-black" ECD, implying a high potential of the application as panchromatic shutter for transparent displays.

Acknowledgement

The authors gratefully acknowledge the Ministry of Science and Technology of Taiwan for the financial support.

References

Published on 12 February 2018. Downloaded by University of Windsor on 19/02/2018 17:33:43.

- 1 Y. Oishi, M. Ishida, M. A. Kakimoto, Y. Imai, T. Kurosaki, J. Polym. Sci. Part A: Polym. Chem. 1992, **30**, 1027.
- 2 K. Ogino, A. Kanegae, R. Yamaguchi, H. Sato, J. Kurjata, Macromol. Rapid Comm. 1999, 20, 103.
- 3 W. L. Yu, J. Pei, W. Huang, A. J. Heeger, *Chem. Commun.* 2000, 681.
- 4 G. S. Liou, S. H. Hsiao, M. Ishida, M. Kakimoto, Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.* 2002, **40**, 3815.
- 5 G. S. Liou, 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, H. T. Chen, *Org. Lett.* 2003, 5, 839.
- 7 S. H. Hsiao, C. W. Chen, G. S. Liou, J. Polym. Sci. Part A: Polym. Chem. 2004, **42**, 3302.
- 8 S. H. Cheng, S. H. Hsiao, T. H. Su, G. S. Liou, *Macromolecules*, 2005, **38**, 307.
- 9 H. J. Yen, G. S. Liou, *Chem. Mater.* 2009, **21**, 4062.
- 10 H. J. Yen, H. Y. Lin, G. S. Liou, Chem. Mater. 2011, 23, 1874.
- 11 H. J. Yen, K. Y. Lin, G. S. Liou, J. Mater. Chem. 2011, 21, 6230.
- 12 H. J. Yen, C. J. Chen, G. S. Liou, *Adv. Funct. Mater.* 2013, **23**, 5307.
- 13 J. H. Wu, G. S. Liou, Adv. Funct. Mater. 2014, 24, 6422.
- 14 D. Weng, Y. C. Shi, J. M. Zheng, C. Y. Xu, Org. Electron. 2016, 34, 139.
- 15 H. J. Yen, C. L. Tsai, S. H. Chen, G. S. Liou, Macromol. Rapid Comm. 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, 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, 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, K. H. Shaughnessy, J. Org. Chem. 2006, 71, 5117.
- 23 L. C. Chen and K. C. Ho, Electrochim. Acta, 2001, 46, 2151.

This journal is © The Royal Society of Chemistry 20xx



DOI: 10.1039/C8CC00224J

Journal Name

ChemComm Accepted Manuscript

Graphic Abstract



A novel panchromatic ambipolar electrochromic device without additional supporting electrolyte was fabricated successfully, and demonstrates high color contrast over the visible light region, fast switching time, and excellent long-term stability.