Supporting Information

Novel Panchromatic Shutter Based on Ambipolar Electrochromic System without Supporting Electrolyte

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Experimental Section

Figure S1. (a) Cyclic voltammetry diagram (scan rate: 50 mV/s) and (b) differential pulse voltammetry diagram (scan rate: 2 mV/s; pulse amplitude: 50 mV; pulse width: 25 ms; pulse period: 0.2 s) of ECD based on TPPA and HV. Devices are ITO glasses with 2 cm x 2 cm active area containing 0.015 M of TPPA and 0.015 M of HV in about 0.05 mL PC with 0.1 M of TBABF$_4$ as the supporting electrolyte.

Figure S2. (a) Cyclic voltammetry diagram (scan rate: 50 mV/s) and (b) differential pulse voltammetry diagram (scan rate: 2 mV/s; pulse amplitude: 50 mV; pulse width: 25 ms; pulse period: 0.2 s) of ECD based on TPB and HV. Devices are ITO glasses with 2 cm x 2 cm active area containing 0.015 M of TPB and 0.015 M of HV in about 0.05 mL PC with 0.1 M of TBABF$_4$ as the supporting electrolyte.

Figure S3. (a) Absorbance spectra and (b) CIE chromaticity diagram for ECD based on TPPA and HV at the corresponding applied potential. Device derived from ITO glasses with 2 cm x 2 cm active area, containing 0.015 M of TPPA and 0.015 M of HV in about 0.05 mL PC with 0.1 M of TBABF$_4$ as the supporting electrolyte.

Figure S4. (a) Absorbance spectra and (b) CIE chromaticity diagram for ECD based on TPB and HV at the corresponding applied potential. Device derived from ITO glasses with 2 cm x 2 cm active area, containing 0.015 M of TPB and 0.015 M of HV in about 0.05 mL PC with 0.1 M of TBABF$_4$ as the supporting electrolyte.

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Figure S11. (a) Current consumption and (b) relation of optical density, charge density, and coloring efficiency (CE) for the ECD based on TPPA/TPB/HV. Device derived from ITO glasses with 2 cm x 2 cm active area, containing 0.01 M of TPPA, 0.03 M of TPB and 0.04 M of HV in about 0.05 mL PC/GBL (1/1) co-solvent without additional supporting electrolyte 14
Experimental Section

Materials

Tri-tert-butylphosphine, propylene carbonate (PC), γ-butyrolactone (GBL), and toluene were stored in the glove box; cesium fluoride, sodium tert-butoxide, sodium tetrafluoroborate and tetra-n-butylammonium bromide were stored in the auto dry box. Heptyl viologen tetrafluoroborate (HV) was acquired by the following process: 4,4'-Bipyridine and excess 1-bromoheptane were dissolved in acetonitrile and reflux for 6 hours. After filtration, the filtered was dissolved in DI water and the excess saturated sodium tetrafluoroborate aqueous solution was added to produce white powder, and recrystallized by ethyl acetate. Tetra-n-butylammonium tetrafluoroborate (TBABF$_4$) was prepared by the following process: Excess saturated sodium tetrafluoroborate aqueous solution was added into a saturated tetra-n-butylammonium bromide aqueous solution, and the white precipitate was filtered and recrystallized by ethyl acetate. The rest of the reagents were received from commercial source.

Monomer Synthesis

$N,N,N',N'$-Tetrakis(4-methoxyphenyl)-1,4-phenylenediamine (TPPA)

\[
\text{AMP} \quad + \quad 4 \quad \text{PhBr} \quad \xrightarrow{\text{Pd$_2$(dba)$_3$, P(tBu)$_3$, NaO}tBu, \text{toluene, reflux, 2 h}} \quad \text{TPPA}
\]

Tris(dibenzylideneacetone)dipalladium(0) (Pd$_2$(dba)$_3$, 187 mg, 0.204 mmol) and tri-tert-butylphosphine (P(tBu)$_3$, 0.10 mL, 0.408 mmol) were added into a 100 mL three-necked round-bottom flask containing 40 mL anhydrous toluene in the glove box preferentially. After stirring at room temperature under nitrogen atmosphere for 10 minutes to undergo the ligand exchange,
4-bromoanisole (5.10 mL, 40.7 mmol) and p-phenylenediamine (1.00 g, 9.25 mmol) were added to the flask sequentially and stirred for another 10 minutes. Sodium tert-butoxide (NaO\text{t-Bu}, 5.33 g, 55.5 mmol) were added into the container and then the solution was refluxed for 3 hours. After cooling to room temperature, the mixture was extracted with water and dichloromethane, and the organic layer was dried over \text{MgSO}_4 and poured into methanol to obtain 4.72 g of pale cream-colored powder (96% yield), mp: 164 °C. FT-IR (KBr, cm\(^{-1}\)): 2833, 1500, 1036, 825. \(^1\)H NMR (400 MHz, DMSO-\text{d}_6, \delta, ppm): 6.94-6.92 (d, 8 H, H\text{b}), 6.87-6.85 (d, 8 H, H\text{c}), 6.74 (s, 4 H, H\text{d}), 3.71 (s, 12 H, H\text{a}).

**Bis(4-methoxyphenyl)amine (BPA)**

![Chemical Structure](image)

Tris(dibenzylideneacetone)dipalladium(0) (Pd\text{2}(\text{dba})_3, 73.2 mg, 0.080 mmol) and tri-tert-butylphosphine (P(\text{t-Bu})_3, 0.040 mL, 0.160 mmol) were added into a 50 mL round-bottom flask containing 20 mL anhydrous toluene in the glove box preferentially. After stirring at room temperature under nitrogen atmosphere for 10 minutes to undergo the ligand exchange, 4-bromoanisole (2.00 mL, 16.0 mmol) was added to the flask sequentially and stirred for another 10 minutes. The solution was then slowly added into another 50 mL round-bottom flask containing \text{p-anisidine} (2.46 g, 20.0 mmol), sodium tert-butoxide (NaO\text{t-Bu}, 1.64 g, 17.0 mmol) and 20 mL anhydrous toluene. The mixture was stirred at room temperature for 4 hours and then extracted with hexane and water. The organic layer was dried over \text{MgSO}_4 and rotary evaporator. The residual was recrystallized from hexane to obtain 1.94 g of pale pink schistose crystal (54% yield), mp: 102-103 °C. FT-IR (KBr, cm\(^{-1}\)): 3420 (-NH), 2839, 1513, 1251, 1032, 830. \(^1\)H NMR (400 MHz, DMSO-\text{d}_6, \delta, ppm): 7.50 (s, 1 H, H\text{d}), 6.92-6.90 (d, 4 H, H\text{b}), 6.82-6.79 (d, 4 H, H\text{c}), 3.68 (s, 6 H, H\text{a}).
*N,N,N',N'-Tetrakis(4-methoxyphenyl)-1,1'-biphenyl-4,4'-diamine (TPB)*

\[
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{O} \\
\text{H} \\
\text{N} \\
\text{O} \\
\text{O}
\end{array}
\quad +
\begin{array}{c}
\text{Br} \\
\text{Br} \\
\text{Pd(OAc)}_2, \text{P(tBu)}_3, \text{NaOtBu}
\end{array}
\quad \text{toluene, reflux, 4 h}
\]

Palladium(II) acetate (Pd(OAc)$_2$, 36 mg, 0.160 mmol) and tri-tert-butylphosphine (P(tBu)$_3$, 0.036 mL, 0.130 mmol) were added into a 50 mL round-bottom flask containing 10 mL anhydrous toluene in the glove box preferentially. BPA (1.91 g, 8.40 mmol), 4,4'-dibromo-1,1'-biphenyl (1.35 g, 4.0 mmol), and sodium tert-butoxide (NaOtBu, 0.960 g, 10.0 mmol) were added into the container sequentially and then the solution was refluxed for 4 hours. After cooling to room temperature, the mixture was extracted with water and dichloromethane. The organic layer was dried over MgSO$_4$ and poured into methanol to obtain 1.95 g of pale yellow powder (80% yield), mp: 159-161 °C. FT-IR (KBr, cm$^{-1}$): 2833, 1604, 1504, 1240, 1035, 822. $^1$H NMR (400 MHz, DMSO-$d_6$, δ, ppm) 7.42-7.39 (d, 4 H, H$_e$), 7.03-7.01 (d, 8 H, H$_b$), 6.92-6.90 (d, 8 H, H$_c$), 6.82-6.79 (d, 4 H, H$_d$), 3.73 (s, 12 H, H$_a$).
Scheme S1. Synthetic procedures of TPPA and TPB

Measurements

Melting point was mainly detected by OptiMelt-Automated Melting Point System and DSC at the scan rate of 5 °C/min. ^1H NMR spectra were recorded on Bruker DPX-400NMR (400 MHz). The definition of splitting pattern is carried out as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Fourier transform infrared (FT-IR) spectra were measured by PerkinElmer Spectrum 100. Electrochemistry was executed with CH Instrument 611B Electrochemical Analyzer or CH Instrument 612C Electrochemical Analyzer. Ultraviolet–visible (UV-Vis) spectra were carried out by Agilent 8453 UV-visible Spectroscopy System. CIELAB data were collected from JASCO V-650 UV-VIS spectrophotometer. Cyclic voltammetry was conducted by using the two-electrode device with 20 mm * 20 mm working area and gap of 120 μm at the scan rate of 50 mV/s. Differential pulse voltammetry was
conducted with the same system at the scan rate of 2 mV/s, pulse amplitude of 50 mV, pulse width of 25 ms and pulse period of 0.2 s. Spectroelectrochemistry and electrochromic properties were carried out by combining CH Instrument 612C Electrochemical Analyzer and Agilent 8453 UV-visible Spectroscopy System the range of 300 and 1100 nm.

**Fabrication of the Electrochromic Device (ECD)**

Thermoset adhesive was first dispensed on an ITO glass (~5 Ω/square) with a 20 mm * 20 mm square shape by full-auto dispenser and a tiny hole was retained. A blank ITO-glass was then pasted onto it and baked at 150 °C for two hours. The gap was controlled by dispersing glass ball with a grain size about 125 μm into the adhesive. The liquid electrolyte (~0.05 mL) containing the electrochromic (EC) materials could be injected into the device by using a sample vacuum encapsulating system. After the injection, the tiny hole was filled up by UV gel. The highly transparent liquid-type electrolyte solution of ECD is based on PC or PC/GBL co-solvent containing EC material and TBABF₄.

**Figure S1.** (a) Cyclic voltammetry diagram (scan rate: 50 mV/s) and (b) differential pulse voltammetry diagram (scan rate: 2 mV/s; pulse amplitude: 50 mV; pulse width: 25 ms; pulse period: 0.2 s) of ECD based on **TPPA** and **HV**. Devices are ITO glasses with 2 cm x 2 cm
active area containing 0.015 M of **TPPA** and 0.015 M of **HV** in about 0.05 mL PC with 0.1 M of TBABF$_4$ as the supporting electrolyte.

**Figure S2.** (a) Cyclic voltammetry diagram (scan rate: 50 mV/s) and (b) differential pulse voltammetry diagram (scan rate: 2 mV/s; pulse amplitude: 50 mV; pulse width: 25 ms; pulse period: 0.2 s) of ECD based on **TPB** and **HV**. Devices are ITO glasses with 2 cm x 2 cm active area containing 0.015 M of **TPB** and 0.015 M of **HV** in about 0.05 mL PC with 0.1 M of TBABF$_4$ as the supporting electrolyte.
Figure S3. (a) Absorbance spectra and (b) CIE chromaticity diagram for ECD based on TPPA and HV at the corresponding applied potential. Device derived from ITO glasses with 2 cm x 2 cm active area, containing 0.015 M of TPPA and 0.015 M of HV in about 0.05 mL PC with 0.1 M of TBABF₄ as the supporting electrolyte.
Figure S4. (a) Absorbance spectra and (b) CIE chromaticity diagram for ECD based on TPB and HV at the corresponding applied potential. Device derived from ITO glasses with 2 cm x 2 cm active area, containing 0.015 M of TPB and 0.015 M of HV in about 0.05 mL PC with 0.1 M of TBABF$_4$ as the supporting electrolyte.
Figure S5. $^1$H NMR spectrum of TPPA in DMSO-$d_6$. 
Figure S6. $^1$H NMR spectrum of BPA in DMSO-$d_6$. 
Figure S7. $^1$H NMR spectrum of TPB in DMSO-$d_6$. 
Figure S8. Differential pulse voltammetry diagram for ECD based on TPPA/TPB/HV at the scan rate of 2 mV/s; pulse amplitude of 50 mV; pulse width of 25 ms; pulse period of 0.2 s. Device derived from ITO glasses with 2 cm x 2 cm active area, containing 0.01 M of TPPA, 0.03 M of TPB and 0.04 M of HV in about 0.05 mL PC/GBL (1/1) co-solvent with 0.16 M of TBABF$_4$ as the supporting electrolyte.

Figure S9. Amplified transmittance spectra of Figure 6b for the TPPA/TPB/HV based ECD at the on-state.
Figure S10. (a) Current consumption and (b) the relation of optical density, charge density, and coloring efficiency (CE) for the ECD based on TPPA/TPB/HV. Device derived from ITO glasses with 2 cm x 2 cm active area, containing 0.01 M of TPPA, 0.03 M of TPB and 0.04 M of HV in about 0.05 mL PC/GBL (1/1) co-solvent with 0.16 M of TBABF$_4$ as the supporting electrolyte. (c) Current consumption and (d) recalculated coloration efficiency for the ECD based on TPA-Vio from our previous work.$^{20}$

Figure S11. (a) Current consumption and (b) relation of optical density, charge density, and coloring efficiency (CE) for the ECD based on TPPA/TPB/HV. Device derived from ITO
glasses with 2 cm x 2 cm active area, containing 0.01 M of TPPA, 0.03 M of TPB and 0.04 M of HV in about 0.05 mL PC/GBL (1/1) co-solvent without additional supporting electrolyte

Reference