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Introduction

Dual-colored 4,4',4",4"'-(cyclobutane-1,2,3,4tetrayl)-tetrabenzoate electrochromic materials with large optical contrast and coloration efficiency⁺

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Nine 4,4',4'',4'''-(cyclobutane-1,2,3,4-tetrayl)tetrabenzoate derivative electrochromic materials have been designed, synthesized, and characterized. Seven compounds displayed dual-colored electrochromism. The required potential and colored states were markedly influenced by substitution. When the substituent was alkyl, colored states of purple and blue were obtained at an applied voltage of -2.3 and -2.6 V, respectively; when the substituent was phenyl with an electron-donating group, colored states of purple bluish and bright blue were obtained at an applied voltage of -2.1 and -2.3 V, respectively; when the substituent was phenyl with an electron-withdrawing group, monocolored state and bad electrochromic properties were obtained. Moreover, electrochromic devices based on most of these compounds show large optical contrast, fast response time, and high coloration efficiency.

The electrochromic phenomenon refers to the color change of a material caused by the application of an electric field, which is reversible and continuously adjustable. Electrochromic materials (ECMs) with significant changes in visible light absorption during electrochromism can find practical application in smart windows,^{1–3} information displays,^{4,5} biological sensors,⁶ and automobile anti-glare devices.⁷

ECMs include inorganic materials (*e.g.*, WO₃^{5,8-13} and Prussian blue^{14,15}), conjugated polymers,^{3,16-21} metal complexes,²²⁻²⁶ and organic small molecules.²⁷⁻³⁰ Compared with inorganic ECMs, organic ECMs have the advantages of easy molecular design, color tunability *via* substitution, high coloration efficiencies, excellent electrochromic switching stability, open circuit memory, and solution processability, and thus have been widely developed.³¹ Among these performances of ECMs, the color change and contrast of the materials are the most intuitive expressions for one's visual observation. Hence, color change and adjustability are important

parameters for evaluating the performance of ECMs. So far, designing ECMs with aesthetically pleasing color states for display applications is a major challenge.²⁷ Therefore, dual- and multi-colored ECMs are desirable. Some researchers have used several methods to obtain dual- and multi-colored ECMs through molecular design^{3,32–38} and introducing two or more electrochromic moieties into materials design.^{15,39–44} For instance, Halas *et al.*³³ reported dual-colored electrochromic devices (ECDs) based on plasmon resonances of polycyclic aromatic hydrocarbon molecules. Liou *et al.*³⁴ reported dual-colored ECDs based on ambipolar triphenylamine derivatives. Moon *et al.*⁴⁰ reported dual-colored ECDs based on mixed monoheptyl viologen and diheptyl viologen.

In recent years, benzoates were reported to exhibit electrochromic properties, in which an ester group was the active center. Some researchers explored the electrochromic properties of di-substituted benzoates including phthalate, isophthalate, and terephthalate, which achieved colorless to trichromatic changes by varying different substituents.^{45–48}

Son *et al.*⁴⁹ reported a series of bis-isophthalate electrochromic systems by changing the length of the conjugated bridge between the two isophthalate groups. Then, they developed a dual-electrochromic system through the combination of a diaryl ketyl radical system with isophthalate-based ECMs.⁵⁰ Research on ester-substituted ECMs has gradually increased due to their excellent solubility and good electrochromic properties.^{39,51–56} Webster and Xu⁵² reported that aromatic oxygen and sulfur diesters exhibited a vibrant colored state during one-electron electrochemical

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[†] Electronic supplementary information (ESI) available: Details of solubility behavior of CBTBAs, NMR and mass spectra, crystal data and structure refinement, molecular orbital diagrams of CBTBAs. CCDC 1936928. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9nj03352a

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reduction. Gong *et al.*⁵³ reported that an azobenzene-4,4'dicarboxylic acid dialkyl ester exhibited good stabilities, welldefined reversible redox processes, electrochromic behavior and reversible photoisomerization properties. Reynolds *et al.*⁵⁴ reported that poly(3,4-propylenedioxythiophenes) with ester-functionalized side chains showed good solubility in environmentally benign solvents, this enables researchers to process conjugated polymers in these solvents without sacrificing the electrochromic performance. However, rare benzoate-based ECMs display dual- or multi-colored properties.⁵⁰

In this work, we reported novel dual-colored benzoate-based ECMs, 4,4',4",4",4"'-(cyclobutane-1,2,3,4-tetrayl)tetrabenzoate derivatives (CBTBAs), in which four esters were the active centers. CBTBAs show excellent solubility in most organic solvents and thus make the manufacture of thin film ECDs easy (see Table S1 in the ESI†). We then fabricated ECDs using the CBTBAs as the active materials and investigated their electrochromic properties; notably, most of them exhibited two distinct color changes, and some of them displayed large optical contrast and coloration efficiency.

Experimental

Materials and instrumentation

Triethoxy(vinyl)silane (AR, 97%), 4-bromobenzoic acid (AR, 98%), palladium acetate (AR, Pd: 46.0–48.0%), polyethylene glycol (PEG 2000), 1,3-propanediamine (AR, 98%), 4-methylphenol (AR, 98%), 4-methoxyphenol (AR, 98%), 4-trifluoromethylphenol (AR, 98%), 4-cyanophenol (AR, 98%), and tetrabutylammonium hexafluorophosphate (TBAPF₆) were purchased from Aladdin Co. Shanghai, China. All of the solvents were of analytic reagent grade and purchased from Chuandong Chemical. TBAPF₆ was recrystallized from a mixed solvent of acetone and ethanol with a volume ratio of 1:4. CH_2Cl_2 , *N*,*N*-dimethylformamide (DMF), and triethylamine were dried with calcium hydride before use.

¹H and ¹³C NMR spectra were recorded using a Bruker 600 MHz spectrometer at room temperature. High-resolution mass spectra were recorded using an Impact II spectrometer, Bruker, Switzerland. Cyclic voltammetry (CV) in this study was performed using a CHI 650 B electrochemical workstation in a three-electrode system. The cell consisted of a working electrode (platinum, Pt), counter electrode (platinum wire), and reference electrode (Ag/AgCl) immersed in 0.1 M TBAPF₆ in DMF as the supporting electrolyte. Before the CV test, the electrolyte solution was purged with nitrogen for 30 min to remove dissolved oxygen; during the CV test, nitrogen was bubbled.

The sandwiched liquid ECDs (35 mm wide \times 40 mm tall \times 0.7 mm thick) based on CBTBAs were assembled according to previous methods using glass coated with indium tin oxide (ITO) and a reflective metal surface (50 Ω sq⁻¹) as the electrodes (Scheme S1 in the ESI†).^{37,47,48} The electrolyte solution was prepared by dissolving CBTBAs (20 mmol), ferrocene (30 mmol, as a counter redox material to stabilize ECD³²), and TBAP (20 mmol) in 5.0 mL DMF, and was then injected into the ECDs using a syringe and sealed with an epoxy adhesive. UV-Vis

spectra were recorded using a UV-4802 spectrophotometer. The CIE (International Commission on Illumination) $L^*a^*b^*$ color space coordinates for the ECDs were measured using a color reader CR-10 plus (Konica Minolta, Inc., Japan). All measurements were performed under ambient conditions.

Synthesis of CBTBAs

CBTBAs (compounds **a**-**i**) were synthesized by the following procedure as shown in Scheme 1.

(E)-4,4'-(Ethylene-1,2-diyl)dibenzoic acid was synthesized based on the literature method with some modifications using PEG as a phase transfer catalyst.⁵⁷ In a 150 mL reaction pot, triethoxy(vinyl)silane (1.61 g, 8.5 mmol) was added to 50 mL of 0.5 M aqueous sodium hydroxide and 4-bromobenzoic acid (2.02 g, 10 mmol) and the mixture was stirred vigorously for 5 min at room temperature. PEG 2000 (4.0 g) and palladium acetate (8 mg) were subsequently added and the reaction pot was placed in a silicone bath at 140 °C for 5 h. The mixture was cooled to room temperature and filtered with silica gel, and 4 M HCl was then added dropwise to pH = 3, resulting in a precipitate. The precipitated solid was filtered and washed with ethanol (3 \times 20 mL) and dried *in vacuo* to give (E)-4,4'-(ethylene-1,2-diyl)dibenzoic acid as a white solid (0.86 g, yield 64%). ¹H NMR (600 MHz, DMSO- d_6) δ (ppm): 12.922 (s, 2H, -COOH), 7.968 (d, 4H, J = 7.8 Hz, Ar-H), 7.765 (d, 4H, J = 7.8 Hz, Ar-H), and 7.490 (s, 2H, -CH=CH-). ¹³C NMR (150 MHz, DMSO-d₆) δ (ppm): 167.47, 141.44, 130.47, 130.39, 130.25, and 127.28.

4,4',4",4'''-(Cyclobutane-1,2,3,4-tetrayl)tetrabenzoic acid was synthesized based on the literature method with some modifications.⁵⁸ A mixture of (*E*)-4,4'-(ethylene-1,2-diyl)dibenzoic acid (1.68 g, 6 mmol), 1,3-propanediamine (0.45 g, 6 mmol), and a few drops of water were ground well for 10 min in an agate mortar. The mixture was dried, placed in two glass slides, irradiated at 365 nm for 48 h, dissolved in water, and acidified with 4 M HCl. The crude product was dried and dissolved in methanol and purified by column chromatography (using petroleum ether : ethyl acetate (v/v) = 1:1 as eluent) to obtain 0.80 g 4,4',4",4'''-(cyclobutane-1,2,3,4-tetrayl)tetrabenzoic acid as a white solid, yield 48%. ¹H NMR (600 MHz, DMSO-*d*₆) δ (ppm): 7.733 (d, 8H, *J* = 7.8 Hz, Ar-H); 7.352 (d, 8H, *J* = 8.4 Hz, Ar-H); and 4.729 (s, 4H, cyclobu-H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ (ppm): 145.27, 136.98, 129.13, 127.90, 126.20, and 70.14.



Scheme 1 Synthetic route for CBTBAs

4,4',4",4'',4'''-(Cyclobutane-1,2,3,4-tetrayl)tetrabenzoic acid (1.07 g, 2.0 mmol) was dissolved in 18 mL of SOCl₂ and 3–4 drops of anhydrous DMF. The mixture was heated at 70 °C for 24 h and an excess of SOCl₂ was removed by distillation to give a yellow solid. The solid was cooled to 5 °C and dissolved in 15 mL CH₂Cl₂ and 5 mL alcohol (or 16 mmol phenol), to which trimethylamine (10 mL) diluted with CH₂Cl₂ (10 mL) was then added dropwise, achieving pH = 8–9 at room temperature for 24 h. The reaction mixture was washed with saturated NaCl aqueous solution (3 × 30 mL), and the organic layer was dried over MgSO₄. After removal of the solvent by rotary evaporation, the residue was purified by column chromatography (petroleum ether: ethyl acetate = 4:1, v/v) to obtain compounds **a–i**.

Tetramethyl 4,4',4",4"'.**(cyclobutane-1,2,3,4-tetrayl)tetrabenzoate** (a). White powder 0.61 g, yield 52%. m.p.: 158.5–159.0 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.819 (d, 8H, *J* = 7.8 Hz, Ar-H), 7.150 (d, 8H, *J* = 8.4 Hz, Ar-H), 4.577 (s, 4H, cyclobu-H), and 3.856 (s, 12H, -COOCH₃). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 166.77, 144.91, 129.62, 128.48, 127.92, 51.99, and 47.48. HRMS: $[M + Na]^+$ calculated for C₃₆H₃₂O₈: 615.1989; found 615.1990.

Tetraethyl 4,4',4",4"'.(cyclobutane-1,2,3,4-tetrayl)tetrabenzoate (b). White powder 0.68 g, yield 52%. m.p. 122.5–122.9 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.831 (d, 8H, *J* = 8.4 Hz, Ar-H), 7.151 (d, 8H, *J* = 8.4 Hz, Ar-H), 4.574 (s, 4H, cyclobu-H), 4.320 (d, 8H, *J* = 7.2 Hz, -COO-CH₂), and 1.356 (t, 12H, *J* = 7.2–14.4 Hz, -CH₃). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 166.34, 144.87, 129.59, 128.80, 127.87, 60.90, 47.55, and 14.30. HRMS: $[M + Na]^+$ calculated for C₄₀H₄₀O₈: 671.2615; found 671.2617.

Tetrabutyl 4,4',4",4'''-(cyclobutane-1,2,3,4-tetrayl)tetrabenzoate (c). White powder 0.61 g, yield 40%. m.p. 97.4–97.8 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.830 (d, 8H, *J* = 8.4 Hz, Ar-H), 7.152 (d, 8H, *J* = 8.4 Hz, Ar-H), 4.571 (s, 4H, cyclobu-H), 4.265 (t, 8H, *J* = 7.2–13.2 Hz, COO–CH₂), 1.713 (t, 8H, *J* = 7.2–15.0 Hz, O–CH₂– CH₂), 1.426–1.464 (m, 8H, *J* = 7.8 Hz, O(CH₂)₂–CH₂–), and 0.963 (d, 12H, *J* = 7.2 Hz, –CH₃). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 166.40, 144.87, 129.60, 127.88, 64.81, 47.58, 30.79, 19.28, and 13.73. HRMS: [M + Na]⁺ calculated for C₄₈H₅₆O₈: 783.3867; found 783.3863.

Tetrabenzyl 4,4',4",4'''-(cyclobutane-1,2,3,4-tetrayl)tetrabenzoate white (d). White powder 0.77 g, yield 43%. m.p. 110.4–110.9 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.853 (d, 8H, *J* = 8.4 Hz, Ar-H), 7.401 (d, 8H, *J* = 7.2 Hz, Ar-H), 7.360 (t, 8H, *J* = 7.2–16.8 Hz, Ar-H), 7.320 (t, 4H, *J* = 7.2–16.8 Hz, Ar-H), 7.132 (d, 8H, *J* = 8.4 Hz, Ar-H), 5.292 (s, 8H, –CH₂–Ar), and 4.549 (s, 4H, cyclobu-H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 166.09, 145.05, 136.03, 129.78, 128.58, 128.45, 128.19, 127.90, 126.98, 66.68, and 47.54. HRMS: $[M + Na]^+$ calculated for C₆₀H₄₈O₈: 919.3241; found 919.3236.

Tetraphenyl 4,4',4",4"''-(cyclobutane-1,2,3,4-tetrayl)tetrabenzoate (e). White powder 1.18 g, yield 70%. m.p. 250.6–251.1 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 8.049 (d, 8H, *J* = 8.4 Hz, Ar-H), 7.431 (t, 8H, *J* = 7.8–16.2 Hz, Ar-H), 7.286 (t, 8H, *J* = 8.4–17.4 Hz, Ar-H), 7.254 (d, 4H, *J* = 6.0 Hz, Ar-H), 7.195 (d, 8H, *J* = 7.8 Hz, Ar-H), and 4.701 (s, 4H, cyclobu-H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 164.84, 150.99, 145.59, 130.35, 129.48, 128.12, 128.09, 125.89, 121.70, and 47.69. HRMS: $[M + K]^+$ calculated for C₅₆H₄₀O₈: 879.2355; found 879.2348. Tetra-*p*-tolyl 4,4',4",4"'-(cyclobutane-1,2,3,4-tetrayl)tetrabenzoate (f). White powder 1.22 g, yield 68%. m.p. 249.6–250.1 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 8.030 (d, 8H, *J* = 8.4 Hz, Ar-H), 7.275 (d, 8H, *J* = 8.4 Hz, Ar-H), 7.200 (d, 8H, *J* = 8.4 Hz, Ar-H), 7.067 (d, 8H, *J* = 8.0 Hz, Ar-H), 4.690 (s, 4H, cyclobu-H), and 2.359 (s, 12H, -CH₃). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 165.05, 148.74, 145.22, 135.51, 130.31, 129.98, 128.15, 128.11, 121.35, 47.67, and 20.88. HRMS: $[M + K]^+$ calculated for C₆₀H₄₈O₈: 935.2981; found 935.2966.

Tetrakis(4-methoxyphenyl) 4,4',4",4"'-(cyclobutane-1,2,3,4tetrayl)tetrabenzoate (g). White powder 1.33 g, yield 69%. m.p. 233.1–233.6 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 8.026 (d, 8H, *J* = 7.8 Hz, Ar-H), 7.275 (d, 8H, *J* = 7.8 Hz, Ar-H), 7.105 (d, 8H, *J* = 9.0 Hz, Ar-H), 6.918 (d, 8H, *J* = 8.4 Hz, Ar-H), 4.690 (s, 4H, cyclobu-H), and 3.808 (s, 12H, $-\text{OCH}_3$). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 165.21, 157.39, 145.32, 144.45, 130.29, 128.12, 122.42, 114.57, 55.64, and 47.67. HRMS: [M + Na]⁺ calculated for C₆₀H₄₈O₁₂: 983.3038; found 983.3023.

Tetrakis(4-(trifluoromethyl)phenyl) 4,4',4",4'''-(cyclobutane-1,2,3,4-tetrayl)tetrabenzoate (h). White powder 1.41 g, yield 63%. m.p. 152.5–153.0 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 8.057 (d, 8H, J = 8.4 Hz, Ar-H), 7.695 (d, 8H, J = 7.2 Hz, Ar-H), 7.326 (t, 16H, J = 6.0–7.2 Hz, Ar-H), and 4.735 (s, 4H, Cyclobu-H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 164.30, 153.43, 145.88, 130.49, 128.35, 127.56, 126.88, 124.80, 123.00, 122.21, and 47.68. HRMS: [M + K]⁺ calculated for C₆₀H₃₆F₁₂O₈: 1151.1850; found 1151.1840.

Tetrakis(4-cyanophenyl) 4,4',4",4'',4'''-(cyclobutane-1,2,3,4-tetrayl)tetrabenzoate (i). White powder 0.97 g, yield 52%. m.p. 147.2– 147.7 °C. ¹H NMR (600 MHz, DMSO-*d*₆) δ (ppm): 7.986 (d, 8H, *J* = 7.8 Hz, Ar-H), 7.965 (d, 8H, *J* = 9.0 Hz, Ar-H), 7.602 (d, 8H, *J* = 8.4 Hz, Ar-H), 7.519 (d, 8H, *J* = 8.4 Hz, Ar-H), and 4.916 (s, 4H, cyclobu-H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ (ppm): 164.25, 154.54, 147.33, 134.50, 130.30, 129.17, 126.80, 123.86, 118.79, 109.40, and 42.69. HRMS: $[M + Na]^+$ calculated for C₆₀H₃₆N₄O₈: 963.2425; found 963.2431.

X-ray crystal structure

Single-crystal X-ray diffraction measurements were carried out using an Agilent SuperNova EosS2 diffractometer using a graphite monochromatic Cu K α radiation ($\lambda = 1.54184$ Å) source. The crystals were kept at 292.0(2) K during data collection. The structures were solved by the ShelXT^{59,60} structure solution program in Olex2⁶¹ and refined using Full-matrix Least Squares based on F2 with program SHELXL-2018^{59,60} within Olex2. Disorder was modelled using standard crystallographic methods including constraints and restraints where necessary.

Results and discussion

Stereochemistry of CBTBAs

Fig. 1 illustrates the X-ray crystal structure of compound **b**, and the crystal data and experimental data are summarized in Table S2 (see the ESI†). CBTBAs exhibited *rctt* stereochemistry, which was consistent with the stereochemistry of 4,4',4'',4'''-(cyclobutane-1,2,3,4-tetrayl)tetrabenzoic acid.⁵⁸



Fig. 1 The X-ray crystal structure of compound ${\bf b}.$ Displacement ellipsoids are set to 30% probability.

Density functional theory calculation

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of CBTBAs were calculated using density functional theory (DFT). The results are listed in Table 1 and shown in Fig. S10 (see the ESI†). As shown in Table 1, the energy gap values (E_{gap}) of compounds **a–d** were very close to 5.22 eV, which indicated that the influence of the alkyl chain length on E_{gap} was negligible. The E_{gap} value of compounds **e–i** was lower than 5.22 eV, and this indicated that the conjugated structure markedly influenced E_{gap} . Compound **g** with an electron-donating group (–OCH₃) showed the lowest value (4.25 eV), and compound **h** with an electron-withdrawing group (–CF₃) showed a much higher value (4.97 eV).

Electrochemical properties

The electrochemical properties of various CBTBAs were investigated by CV at a scan rate of 100 mV s⁻¹ in DMF (1.0 mmol L⁻¹) using TBAPF₆ (50.0 mmol L⁻¹) as a supporting electrolyte. The potential was cycled from -2.20 V to +1.05 V vs. Ag/AgCl. The results are shown in Fig. 2, Fig. S11 (see the ESI†), and Table 2. When R was an alkyl chain (compounds **a**-**d**), the CV traces were nearly identical in shape, and all contained four cathodic peaks and three anodic peaks. Taking compound **b** as an example, as shown in Fig. 2A, a weak cathodic peak at around -0.78 V (1) vs. Ag/AgCl was observed after a few scans, and the intensity

Table 1 HOMO and LUMO energy levels, as well as $E_{\rm gap}$ of CBTBAs determined by DFT calculations

Compound	HOMO (eV)	LUMO (eV)	$E_{\rm gap}$ (eV)
a	-6.61	-1.39	5.22
b	-6.57	-1.34	5.23
c	-6.55	-1.34	5.21
d	-6.56	-1.35	5.21
e	-6.49	-1.63	4.86
f	-6.23	-1.56	4.67
g	-5.74	-1.49	4.25
h	-6.99	-2.02	4.97
i	-7.08	-2.25	4.83



Fig. 2 Cyclic voltammograms of 1 mmol L⁻¹ CBTBAs cycled 100 times between -2.20 and 1.05 V vs. Ag/AgCl in 50 mmol L⁻¹ TBABF₆/DMF at 100 mV s⁻¹ for compounds **b** (A), **f** (D), **h** (E), and **i** (F). Cyclic voltammograms of 1 mmol L⁻¹ compound **b** cycled 100 times between -1.90 and 1.05 V in 50 mmol L⁻¹ TBAPF₆/DMF at 100 mV s⁻¹ (B). The relationship between the peak current and the square root of scan rate of compound **b** (C).

Table 2The E_{pa} and E_{pc} data of compounds $\mathbf{a}-\mathbf{i}$

Compound	$E_{\rm pa}$ (V vs. Ag/AgCl)	$E_{\rm pc}$ (V vs. Ag/AgCl)
a b c d e f g h	$\begin{array}{c} -0.15, -1.40, -1.60, -0.14, -1.41, -1.62, -0.13, -1.40, -1.61, -0.13, -1.36, -1.55, -0.13, -1.36, -1.55, -0.127, -1.42, -0.127, -1.43, -0.130, -1.43, -0.1.30, -1.43, -0.1.24, -$	$\begin{array}{c} -0.78, -1.48, -1.68, -2.04\\ -0.78, -1.49, -1.70, -2.04\\ -0.79, -1.49, -1.69, -2.05\\ -0.79, -1.46, -1.65, -2.01\\ -0.80, -1.35, -1.49, -1.89\\ -0.82, -1.36, -1.51, -1.91\\ -0.80, -1.36, -1.52, -1.91\\ -0.84, -1.36, -1.88\end{array}$
i	—	-0.80, -2.03

gradually increased as more scans were performed. This was probably attributed to the reduction of a reaction product of the later processes. The quasi-reversible redox couple at *ca.* -1.49 V (2) and -1.41 V (2') was ascribed to the one-electron redox reaction between CBTBAs and CBTBAs^{-•}, and the quasi-reversible redox couple at *ca.* -1.70 V (3) and -1.62 V (3') *vs.* Ag/AgCl was ascribed to the one-electron redox reaction between CBTBAs^{-•}. The fourth cathodic peak at -2.04 V (4) *vs.* Ag/AgCl was stronger than the cathodic peaks at 2 and 3; however, the corresponding anodic peak (4') was weak.

This indicates that it is more likely to be a multi-electron process that presumably leads to reduction of CBTBAs^{2–} to CBTBAs^{4–}. To illustrate the relationship between process 4 and processes 1–3, a CV test without process 4 was scanned from -1.90 to +1.05 V *vs.* Ag/AgCl (Fig. 2B). Both the anodic (1', 2', and 3') and cathodic peaks (1, 2, and 3) became weak.



Scheme 2 Redox mechanism and states of CBTBAs in an electrolyte solution.

The result illustrated that the reduction product, CBTBAs^{4–}, was partially decomposed to CBTBAs^{-•}, CBTBAs²⁻, and other compounds. In order to investigate that the processes 2 and 3 are diffusion-controlled or adsorption-controlled, CVs of compound **b** were performed in 50.0 mmol L^{-1} TBAPF₆ solution at different potential scan rates (20, 50, 80, 100, and 120 mV s⁻¹). The linear relationship of peak current versus square root of scan rates indicated that they are diffusion-controlled (Fig. 2C). When R was phenyl (compounds e-i), the substituents on benzene markedly influenced the electrochemical properties. For electron-donating substituents (compounds e-g), the CV curves were nearly similar to those of compounds **a-d**, and this indicates that they have the same redox mechanism. However, the anodic peak potential (E_{pa}) and cathodic peak potential $(E_{\rm pc})$ of the two reversible redox couples and the fourth cathodic peak were higher (Table 2), namely the redox reaction was easier. Taking compound **f** as an example (Fig. 2D), the two quasi-reversible redox couples were observed at ca. -1.36 V (2) and -1.29 V (2'), -1.51 V (3) and -1.43 V (3') vs. Ag/AgCl, respectively. This result was probably attributed to the enlarged conjugated structures of compounds e-g compared to those of compounds a-d. This was consistent with the DFT calculations, compounds e-g have a lower E_{gap} than compounds a-d(Table 1). The redox mechanism and states of compounds a-g are shown in Scheme 2. For electron-withdrawing substituents (compounds h and i), their CV curves were different. For compound h, only one reversible redox couple appeared (Fig. 2E); for compound i, no reversible redox couple was observed (Fig. 2F). This result demonstrates that the electron-withdrawing substituents were not beneficial for the electrochemical properties of CBTBAs possibly due to the reduced electron-donating characteristics of benzene.

Optical properties

Spectroelectrochemical analysis was carried out to study the optical switch and color change of electrochromic materials with different potentials using a two-electrode configuration,^{32,62} and the absorption spectra and photographs of CBTBA-based ECDs are shown in Fig. 3 and Fig. S12 in the ESI.† At an applied potential of 0.0 V, all compounds displayed a weak and broad absorption band at *ca.* 440 nm due to the π - π * transition and



Fig. 3 UV-Vis absorption spectra of compounds **b** (A), **f** (B), **h** (C), and **i** (D) with a concentration of 20 mmol L^{-1} on indium tin oxide-coated glass at different potentials. (E) Photographs of electrochromic devices containing compounds **a**–**h** in their bleached and colored states.

colorless state. When different negative potentials were applied, different phenomena dependent on R were observed.

When R was an alkyl chain (compounds a-d), they displayed similar absorption spectra and colored states. Taking compound **b** as an example (Fig. 3A), as the applied potential decreased to -2.0 V, a maximum absorption peak was located at 576 nm and there were also two absorption peaks at 520 and 846 nm, and at the same time the ECD showed a color state of purple. The color change was ascribed to the reduction of CBTBAs to CBTBAs^{-•}. The absorption intensity increased as the applied potential decreased, and saturated at an applied voltage of -2.3 V. As the applied potential further decreased to -2.4 V, a new absorption peak at *ca.* 626 nm appeared, and the ECD displayed a second colored state of blue owing to the reduction of CBTBAs^{-•} to CBTBAs²⁻, which was consistent with the CV result. Owing to the poorer conductivity of the ITO electrode in ECDs compared with that of in the Pt electrode in CV, the voltage was much more negative due to the overpotential.³² The required potentials of CBTBAs (-2.1 V for purple bluish and -2.3 Vfor bright blue) are slightly lower than 46,53,55 or comparable to 47-50,63 previously reported ester-based organic ECMs.

Molecules with other reactive centers or a greater conjugation degree may realize a low voltage switch.³⁷ When R was an electrondonating phenyl group (compounds **e**–**g**), a similar change in the UV-Vis absorption spectra was observed, but the applied potentials

Table 3 The CIE $L^*a^*b^*$ coordinate values of all the ECDs based on compounds $\mathbf{a}-\mathbf{i}$

Compound	$L^*a^*b^*$				
	0.0 V	-2.3 V	-2.6 V		
a	64*-5*10	32*20*-27	24*18*-44		
b	64*-4*8	33*17*-23	30*11*-39		
с	67*-5*12	28*20*-31	20*20*-36		
d	67*-4*12	36*14*-27	25*14*-44		
e	66*-4*10	$37*4*-26^{a}$	$32*3*-39^{b}$		
f	69*-5*11	$42*0*-23^{a}$	$32^{*}4^{*}-43^{b}$		
g	64*-6*16	33*5*-27 ^a	$27*9*-44^{b}$		
ĥ	$64^{*}-4^{*}-5$	_	$34*4*-46^{c}$		
i	57*-7*32	—	$56^{*}-6^{*}26^{c}$		

" The applied voltage is -2.1 V." The applied voltage is -2.3 V." The applied voltage is -2.6 V.

for the first and second colored states were -1.9 and -2.1 V, respectively, and all absorption peaks were slightly red-shifted, which was caused by the increased degree of conjugation (Fig. 3B and Fig. S12, ESI[†]). This was consistent with the results of DFT calculation and CV. The two colored states were purple bluish and bright blue. For the ECD based on h, only one absorption peak at 590 nm (Fig. 3C) and one colored state (bright blue) (Fig. 3E) were observed, and this was also consistent with the CV result in which one reversible redox couple was obtained. For the ECD based on i, no obvious absorption peaks appeared as the applied voltage decreased to -2.8 V (Fig. 3D) and no colored state was obtained (Fig. S12F, ESI[†]). Moreover, a significant aging phenomenon occurred, indicating that the electron-withdrawing effect was not beneficial to the electrochromic properties of CBTBAs due to the decreased conjugation. The chromaticity coordinates for the ECDs based on compounds a-i in the bleached and colored states are shown in Table 3.

Optical contrast and electrochromic switching

The electrochromic switching properties of ECDs based on compounds a-h were investigated by studying the change in optical contrast (ΔT %) between the colored and bleached states over time via repeated potential steps between -2.3 and +2.3 V and -2.6 and +2.6 V for compounds a-d, -2.1 and +2.1 V and -2.3 and +2.3 V for compounds e-g, and -2.6 and +2.6 V for compound h with a residence time of 4 s at λ_{max} (Fig. 4 and Fig. S13 in the ESI[†]). In the first colored state, the optical contrast was 75.16%, 68.17%, 81.38%, 54.98%, 65.50%, 76.54%, 76.37%, and 47.59% for compounds a, b, c, d, e, f, g, and h, respectively. In the second colored state, the optical contrast was 81.13%, 82.66%, 80.64%, 64.93%, 70.51%, 80.78%, and 78.33% for compounds a, b, c, d, e, f, and g, respectively. Compared to previous reports about organic ECMs,^{27,36,37,51,53,54,64} most of the CBTBAs showed higher color contrast of >70%. When R was an alkyl chain (compounds a-d), the first colored state showed better switching stability than the second colored state (Fig. 4C). When R was an electron-donating phenyl group (compounds e-g), both the first and second colored states showed good switching stabilities (Fig. 4D). When R was the electron-withdrawing phenyl group (compound h), the switching stability was bad (Fig. S13F, ESI⁺). This result demonstrated that R markedly influenced the switching stability of CBTBAs.



Fig. 4 Electrochromic switching responses of ECDs monitored at λ_{max} for compounds **a**-**d** between -2.3 V and +2.3 V (the black curve) and between -2.6 V and +2.6 V (the red curve) with a residence time of 4 s (A), for compounds **e**-**h** between -2.1 V and +2.1 V (the black curve) and between -2.3 V and +2.3 V (the red curve) with a residence time of 4 s (B). Electrochromic switching responses of devices with compounds **a** (C) and **f** (D) at a monochromatic wavelength as a function of time between ± 2.3 V and ± 2.6 V for compound **a** and ± 2.1 V and ± 2.3 V for compound **f**.

The response times are defined as the time to reach 95% of the whole change in transmittance between the steady bleached and colored states at the maximum absorption wavelength.³⁷ As shown in Fig. 5 and Tables 4 and 5, each CBTBA compound exhibits a bleaching time of less than 1 s and a coloration time of 1–2 s to reach 95% of a full-contrast switch (t_{95}) at two coloring voltages. A faster response time can be found for compounds **a–d** when the substituent was an alkyl chain.

The coloration efficiency (CE; η) indicates the change in optical density at the monitoring wavelength with the inserted



Fig. 5 Response times of ECDs based on compounds $\mathbf{a}-\mathbf{d}$ at ± 2.3 V and $\mathbf{e}-\mathbf{g}$ at ± 2.1 V (A), and $\mathbf{a}-\mathbf{d}$ and \mathbf{h} at ± 2.6 V, and $\mathbf{e}-\mathbf{g}$ at ± 2.3 V (B). Chronoamperometry curve and the corresponding *in situ* transmittance curve (C) and optical density *versus* charge density (D) of the ECD based on compound \mathbf{a} .

Table 4 Electrochromic properties of compounds a-d between ± 2.3 V and ± 2.6 V at the maximum absorption wavelength

Compound		a	b	с	d
T _c	$\pm 2.3 \text{ V}$	1.27	1.17	1.71	1.56
	$\pm 2.6 \text{ V}$	1.29	1.43	1.47	1.43
$T_{\rm b}$	$\pm 2.3 \text{ V}$	0.46	0.56	0.96	0.88
	$\pm 2.6 \text{ V}$	0.88	0.80	0.92	0.85
CE (η) (cm ² C ⁻¹)	± 2.6 V	2434	2827	3697	576

Table 5 Electrochromic properties of compounds e-h between ± 2.1 V and ± 2.3 V at the maximum absorption wavelength

Compound		e	f	g	h (±2.6 V)
T _c	$\pm 2.1 \text{ V}$	1.60	1.89	1.90	1.78
	$\pm 2.3 \text{ V}$	1.80	1.82	2.19	
Th	$\pm 2.1 \text{ V}$	0.97	0.98	0.90	0.75
	$\pm 2.3 \text{ V}$	0.61	0.97	0.95	
$CE(\eta) (cm^2 C^{-1})$	$\pm 2.3 \text{ V}$	2555	3882	1422	786

charge per area, which can be calculated via optical density using the equation $\eta = \Delta OD/Q_d$, where $\Delta OD = \log\left(\frac{T_b}{T_c}\right) (T_c \text{ and }$ $T_{\rm b}$ denote the light transmittance of the colored and bleached states of the ECD at a specific wavelength), and Q_{d} is the injected/extraction charge per unit area during a redox step. The CE values of compounds **a-h** were obtained by fitting the slope of linear plots concerning ΔOD vs. Q according to the method reported by Xiao.^{65,66} Taking compound a as an example, Fig. 5C shows the chronoamperometry curve and the corresponding in situ transmittance curve. Fig. 5D shows the optical density versus charge density calculated from the data shown in Fig. 5C. Based on this method, the CE values of CBTBAs estimated from the data are shown in Tables 4 and 5. Most of these compounds showed high CE. The coloration efficiency of compounds $\mathbf{a-c}$ at ± 2.6 V and $\mathbf{e-g}$ at ± 2.3 V is above 1000 $\text{cm}^2 \text{ C}^{-1}$.

Conclusions

In this study, a series of novel dual-colored 4,4',4",4"'-(cyclobutane-1,2,3,4-tetrayl)tetrabenzoate (compounds a-g) electrochromic materials was synthesized and fabricated into ECDs. All compounds show excellent solubility and are soluble in most organic solvents and provide a path for the manufacture of thin film ECDs. By introducing alkyl groups with different chain lengths and phenyl groups with different electrondonating abilities, the electrochromic switch stability and color change of CBTBAs are significantly affected. Compounds a-g exhibited two colored states at different voltages. When the applied voltages were 0.0, -2.3, and -2.6 V, compounds a-d changed from colorless to purple and blue; when the applied voltages were 0.0, -2.1, and -2.3 V, compounds e-g changed from colorless to purple bluish and bright blue. Most of them displayed high optical contrast and coloration efficiency. Improvement of the switching stability is under investigation.

Conflicts of interest

There are no conflicts to declare.

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