

Flexible electrofluorochromic devices with the highest contrast ratio based on aggregation-enhanced emission (AEE)-active cyanotriphenylamine-based polymers†

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Hung-Ju Yen and Guey-Sheng Liou*

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Flexible electrofluorochromic devices were prepared from two electrochromic and AEE-active (AEE: aggregation-enhanced emission) cyanoarylamine-containing high-performance polymers, exhibiting the highest contrast ratio (I_f/I_{f0}) of 151.9 at a low working potential.

Electrofluorochromism (EFC) deals with the electrically driven reversible optical changes in the fluorescence.¹ Reversible switching of the optical status by electrochemical or photochemical conversion of UV-vis or photoluminescence spectra is a desirable field of investigation in optoelectronic devices such as displays, sensors, or optical memories.² In particular, fluorescent high-performance polymers are promising candidates for application in EFC devices because of their excellent thermal stability, high mechanical strength, low flammability, good chemical and radiation resistance, and good electronic properties.³

Bifunctional fluorescent molecular switches appeared in the late 1990s and early 2000s, the first example being published by Lehn,⁴ who used a quinone redox state to switch a ruthenium-bipyridine complex on and off. In 2006, Audebert and Kim⁵ published the first example of an electrochemically driven passive fluorescent flat device ("electrofluorochromic" window) using tetrazine containing material. Hitherto, several EFC devices containing fluorescent naphthalimide-tetrazine, ferrocene-pyrene disubstituted azine, poly(oxadiazole), and triphenylamine based polyfluorene have been synthesized and investigated.¹ However, these EFC devices could only reveal contrast ratios (I_f/I_{f0}) of less than 22% due to the low photoluminescent intensity of the EFC materials thus restricting their fluorescent/non-fluorescent on/off ratio.

Recently, aggregation-enhanced emission (AEE), opposite of the aggregation-caused quenching (ACQ) effect observed in most conventional chromophores, paved a new avenue for the design and synthesis of efficient solid-state emitters.⁶

Under this design concept, we reported two newly AEE-active cyanoarylamine-containing high-performance polymers, polyimide CN-PI and polyamide CN-PA, which have the AEE feature and are highly emissive in the solid state with a PL quantum yield of up to 65%.⁷ The results demonstrated a feasible approach to prepare efficient luminescent materials for optoelectronic applications. In addition, triarylamine derivatives are well known for their photo- and electroactive properties that have potential for optoelectronic applications, such as photoconductors, hole-transporters, light-emitters, and memory devices.⁵ Electron-rich triarylamines can also be easily oxidized to form stable radical cations, and the oxidation process is always associated with a noticeable change in coloration and broad absorption in the visible or near-infrared region.

In this communication, we therefore utilized the AEE-active and electrochromic (EC) cyanoarylamine-containing polymers, polyimide CN-PI and polyamide CN-PA, for the fabrication of the EFC devices (Fig. 1a). Using the excellent combination of the individual features in EC and fluorescent properties, a high contrast ratio could be achieved and the flexible EFC devices were further fabricated (Fig. 1b).

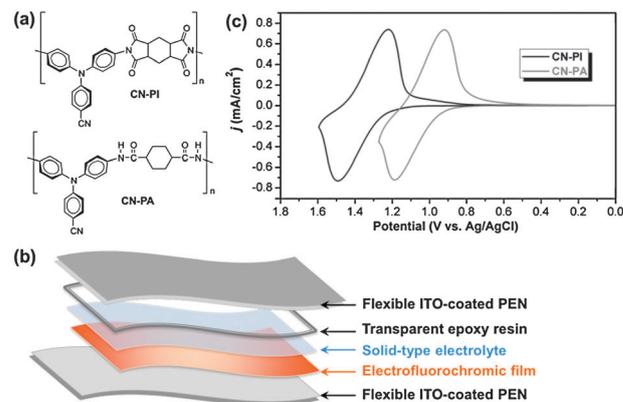


Fig. 1 (a) Chemical structures of CN-PI and CN-PA, (b) schematic diagram of flexible EFC device based on single-layer EFC polymer, and (c) cyclic voltammetry of polymer films on an ITO-coated glass substrate 0.1 M TBAP/acetonitrile at a scan rate of 50 mV s⁻¹.

Functional Polymeric Materials Laboratory, Institute of Polymer Science and Engineering, National Taiwan University, 1 Roosevelt Road, 4th Sec., Taipei 10617, Taiwan. E-mail: gsliou@ntu.edu.tw; Fax: +886-2-33665237; Tel: +886-2-33665315
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The electrochemical properties of polymers were investigated by cyclic voltammetry (CV) conducted by a cast film on an indium-tin oxide (ITO)-coated glass slide as the working electrode in anhydrous acetonitrile (CH_3CN), using 0.1 M of tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte in a nitrogen atmosphere. Typical CV diagrams for the polymers are shown in Fig. 1c, both revealing one reversible oxidation redox couple. During the electrochemical oxidation of the polymer thin films, the color changed from colorless to bluish-green and purple for CN-PI and CN-PA, respectively.

Spectroelectrochemical experiments were used to evaluate the optical properties of the EC films. For the investigation, polymer film was prepared in the same manner as CV, and a homemade electrochemical cell was built from a commercial ultraviolet (UV)-visible cuvette. The cell was placed in the optical path of the sample light beam in a UV-vis-NIR spectrophotometer, which allowed us to acquire electronic absorption spectra under potential control. The typical spectroelectrochemical spectra and three-dimensional transmittance-wavelength-applied potential correlations of polymers CN-PI and CN-PA were presented in Fig. 2, which were reversible and associated with strong color changes.

For polyimide CN-PI, in the neutral form (0 V), the film exhibited strong absorption at around 316 nm, characteristic for triarylamine, but it was highly transparent in the visible region. Upon oxidation (increasing the applied voltage from 0 to 1.60 V), the intensity of the absorption peak at 316 nm gradually decreased while new peaks at 367 and 735 nm gradually increased in intensity due to the formation of monocation radicals of CN-PI. Meanwhile, the color of the film changed from colorless (L^* , 97; a^* , -2; b^* , 3) to bluish-green (L^* , 55; a^* , -18; b^* , -6) with a high optical transmittance change ($\Delta\%T$) of 87% at 735 nm.

On the other hand, the spectroelectrochemical behavior of the polyamide CN-PA film shown in Fig. 2b also exhibited

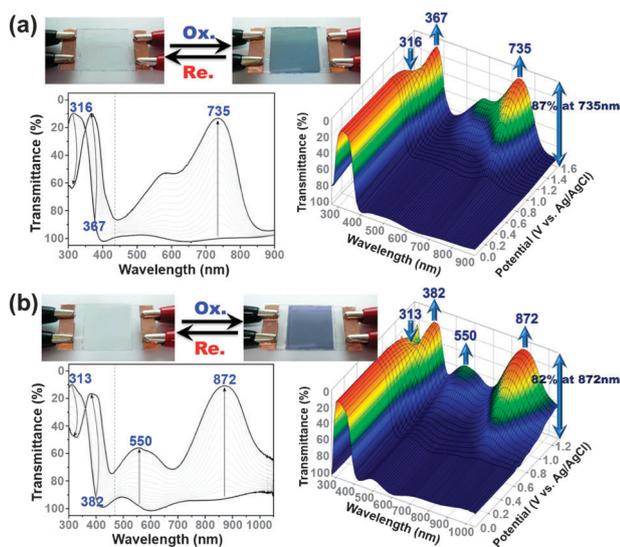


Fig. 2 EC behavior (left) and 3-D spectroelectrochemical behavior (right) from 0.00 (V vs. Ag/AgCl) to the oxidized state of (a) CN-PI and (b) CN-PA thin films (150 ± 10 nm in thickness) on the ITO-coated glass substrate.

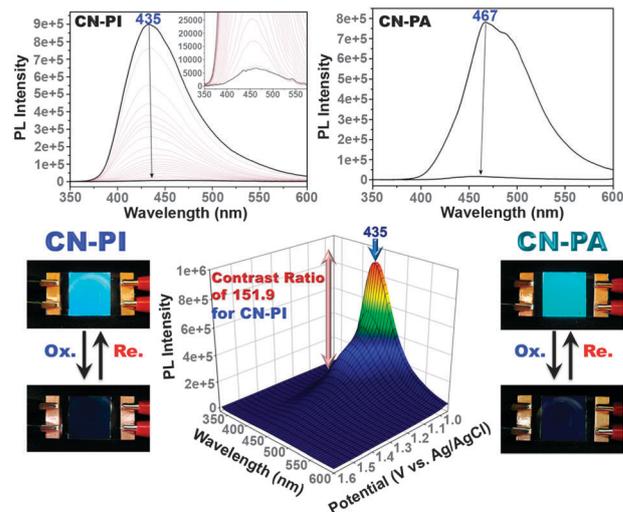


Fig. 3 Fluorescence intensity changes and electrofluorochromic behavior of the EFC device using CN-PI and CN-PA (150 ± 10 nm in thickness) as active layers.

strong absorption at around 313 nm in the neutral form (0 V) that decreased and new peaks at 382, 550, and 872 nm grew steadily upon electrochemical oxidation (increasing the applied voltage from 0 to 1.30 V). From the inset shown in Fig. 2b, the film switched from colorless (L^* , 96; a^* , 3; b^* , -2) to purple (L^* , 50; a^* , 10; b^* , -28) with a high optical transmittance change ($\Delta\%T$) of 85%. Besides, the film colorations are distributed homogeneously across the polymer film and reveal modest electrochemical stability.

The EFC devices of CN-PI and CN-PA emit blue and green light under UV excitation, respectively. In preliminary studies, the EFC device was used in the experiments of fluorescence intensity changes with the applied electrical positive potentials (Fig. 3). Upon increasing the applied voltage from 0 to 1.60 V, the fluorescence of CN-PI was extinguished to dark. The monocation radical of CN-PI is known to have an absorption band at around 350–800 nm, acting as an effective fluorescence quencher so that the fluorescence is efficiently quenched. The fluorescence intensity changes occurred without a shift of the emission band with the potential changes, indicating that the fluorescence quenching originated from the electrochemical oxidation of the triphenylamine unit to its monocation radical form without producing any side products. The polymer film returned back to its original fluorescence when the potential was subsequently set back to 0 V. In addition, the CN-PA shows a similar oxidative fluorescence quenching process (Fig. 3).

Notably, the triarylamine-based CN-PI and CN-PA having an AEE feature are highly emissive in the solid state, which could be quenched upon application of step potentials with relatively high contrast ratios (I_f/I_{f0}) of 151.9 and 51.3, respectively, implying that the judicious combination of the AEE and EC features is an essential approach to EFC devices. Fluorescence switching of an EFC device using CN-PA as the active layer is provided in Fig. S1 (ESI[†]) as the stability and reproducibility measurement of this device. Due to the moderate stability of the prepared EFC device, the structure modification is in progress to enhance the long-term durability for practical

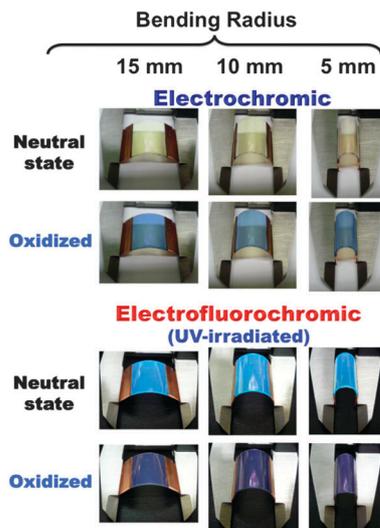


Fig. 4 EC and EFC behaviors of the single-layer flexible ITO-coated PEN EFC device using polyimide **CN-PI** (150 ± 10 nm in thickness) as the active layer in various bent and oxidative states.

applications. Furthermore, we also fabricated single layer flexible EFC cells based on the polyimide **CN-PI** for bending investigations (Fig. 4). The severe bending of the EFC device at various curvature radii of 15, 10, and 5 mm does not degrade the EC and EFC behaviors, revealing that the flexible EFC device is reliable even when the substrate is severely bent. We believe that optimization could further improve the device performance and fully explore the potential of the EFC materials.

In summary, the flexible electrofluoro-chromic devices with the highest contrast ratio were successfully constructed from two AEE-active and EC cyanoarylamine-containing high-performance polymers, polyimide **CN-PI** and polyamide **CN-PA**. The electrochemical fluorescence switching of **CN-PI** from a fluorescent neutral state to a non-fluorescent monocation radical state at a low working potential, giving rise to the highest contrast ratio (I_f/I_{f0}) of 151.9 to the best of our knowledge. These results demonstrate that incorporation of the EC and AEE-active cyanoarylamine chromophore into high-performance polymers is a feasible approach to prepare efficient EFC devices.

Materials: the polyimide **CN-PI** and polyamide **CN-PA** were prepared according to a previously reported procedure.⁷ TBAP (Acros) was recrystallized twice by ethyl acetate in a nitrogen atmosphere and then dried *in vacuo* prior to use. All other reagents were used as received from commercial sources.

Fabrication of the flexible electrofluoro-chromic device: an EFC polymer film was prepared by coating solution of the polymers (50 mg mL^{-1} in DMAc) onto ITO coated poly(ethylene 2,6-naphthalate) (PEN) ($20 \text{ mm} \times 30 \text{ mm} \times 0.3 \text{ mm}$, $20\text{--}30 \Omega$ per square) as depicted in Fig. 1b. The ITO coated PEN used for the EFC device was cleaned by ultrasonication with water, acetone, and isopropanol, each for 15 min. The polymer was spin-coated onto an active area ($20 \text{ mm} \times 20 \text{ mm}$) and then dried in vacuum. A gel electrolyte based on poly(methyl methacrylate) (PMMA) (M_w : 350 000) and LiClO_4 was plasticized with propylene

carbonate (5 g) to form a highly transparent and conductive gel. PMMA (3 g) was dissolved in dry acetonitrile (15 g), and LiClO_4 (0.3 g) was added to the polymer solution as the supporting electrolyte. The gel electrolyte was spread on the polymer-coated side of the electrode, and the electrodes were sandwiched. Finally, an epoxy resin was used to seal the device.

Measurements: Ultraviolet-visible (UV-Vis) spectra of the polymer films were recorded on a Hewlett-Packard 8453 UV-Visible diode array spectrometer. Photoluminescence (PL) spectra and CIE 1931 coordinates were measured using a Fluorolog-3 spectrofluorometer. All spectra were obtained by averaging five scans. Electrochemistry was performed using a CH Instruments 611B electrochemical analyzer. Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downwards. Cyclic voltammetry (CV) was conducted with the use of a three-electrode cell in which ITO (polymer films area about $0.5 \text{ cm} \times 1.2 \text{ cm}$) was used as a working electrode. A platinum wire was used as an auxiliary electrode. All cell potentials were obtained using a homemade Ag/AgCl , KCl (sat.) reference electrode. Spectroelectrochemical experiments were carried out in a cell built from a 1 cm commercial UV-visible cuvette using a Hewlett-Packard 8453 UV-Visible diode array spectrophotometer. The ITO-coated glass slide was used as the working electrode, a platinum wire as the counter electrode, and a Ag/AgCl cell as the reference electrode. The thickness of the polymer thin film was measured by an alpha-step profilometer (Kosaka Lab., Surfcoorder ET3000, Japan). Colorimetric measurements were obtained using JASCO V-650 spectrophotometer and the results are expressed in terms of lightness (L^*) and color coordinates (a^* , b^*).

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