Tunable Electrofluorochromic Device from Electrochemically Controlled Complementary Fluorescent Conjugated Polymer Films

Cheng-Po Kuo,[†] Chiou-Ling Chang,[‡] Chih-Wei Hu,[§] Ching-Nan Chuang,[||] Kuo-Chuan Ho,*[,§,||] and Man-kit Leung*[,‡,||]

[†]Material and Chemical Research Laboratories, Industrial Technology Research Institute, Hsinchu 300, Hsinchu 31040, Taiwan, R.O.C.

[‡]Department of Chemistry, [§]Department of Chemical Engineering, and [||]Institute of Polymer Science and Engineering, National Taiwan University, 1 Roosevelt Road, Section 4, Taipei 10617, Taiwan, R.O.C.

S Supporting Information

ABSTRACT: The fluorescent behavior of the electrofluorochromic devices (Type I) of greenish-yellow emitting **P1** and blue emitting **P2** can be reversibly switched between the nonfluorescent (oxidized) state and the fluorescent (neutral) state with a superb on/off ratio of 23.8 and 21.9, respectively. Moreover, a tunable electrofluorochromic device (Type II) based on two **P1** and **P2** polymeric layers that are coated individually on two independent ITO electrodes shows switchable blue-white-(greenish-yellow) multifluorescence states.
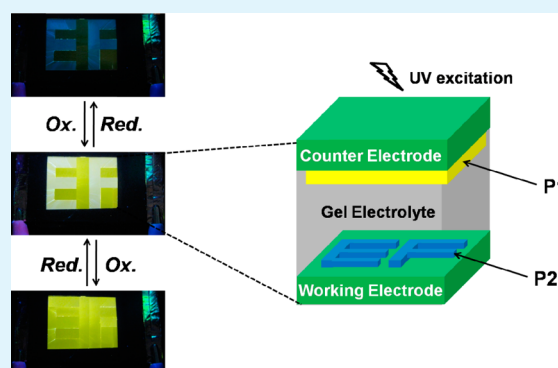
INTRODUCTION

Electrofluorochromism (EFC), which is defined as the reversible fluorescence (FL) change induced by electrochemical oxidation or reduction, has recently attracted a lot of attention. Various EFC materials utilizing organic/inorganic hybrid thin films, organic metal complexes, organic molecules, and fluorescent polymers have been explored.[1−15] A pioneering example of a small molecule electrofluorochromic device (EFCD) derived from tetrazine molecule was reported by Audebert and Kim et al.[5] In addition, Audebert et al. have recently published reports describing the EFC molecules that are composed of two fluorophores, an electron-rich triphenylamine unit, and an electron-poor tetrazine unit. The bichromophores are not fluorescent in the neutral state due to the photoinduced electron transfer quenching mechanism from the triphenylamine unit to the tetrazine unit. The fluorescence can be restored by oxidation of the triphenylamine moiety.[14,16] Moreover, conjugated fluorescent polymers are another kind of promising materials for EFCDs; their sensitivity on FL quenching can be amplified through efficient electronic delocalization and rapid migration of excitons along the π-conjugated backbone.[17−19] We have developed novel p-type triphenylamine-based polymeric EFCDs, leading to a two-state switchable device.[20,21]

A further challenge is to establish multicolor EFCDs that consist of several different "on/off" states and display different color emission. To achieve this purpose, one might perceive that each fluorophore in a multifluorophore mixture should solely responses to a specific electrical potential (EP). The fluorophores with different color emission could therefore be switched on and off by precise electrical voltage control.[7] However, this might be difficult to control in some cases due to complicated energy transfer mechanisms between molecules in solid films.

In the present article, we report another alternative of establishing a multifluorescent device composed of complementary FL layers, in which each fluorescent layer could be individually controlled. The concept of using complementary layers for electrochromic devices has been widely used.[22−27] Kim et al. recently reported the use of oxidation of polyfluorene and reduction of poly(3,4-propylenedioxythiphene) to construct an EFCD that shows switching emission between white, cyan, and blue.[28] To provide wider emission color range, higher on/off ratio, and faster switching performance, we adopt herein a greenish-yellow emitting **P1** and a blue emitting **P2** as our complementary partners for our multicolor EFCD (Scheme 1). Fluorene-based conjugated polymers (PFs) are of great interest as light-emitting materials because of their high photo-

Scheme 1. (a) Chemical Structures of P1 and P2. (b) Schematic Illustration of the Creation of a Multicolor EFCD (Type II)
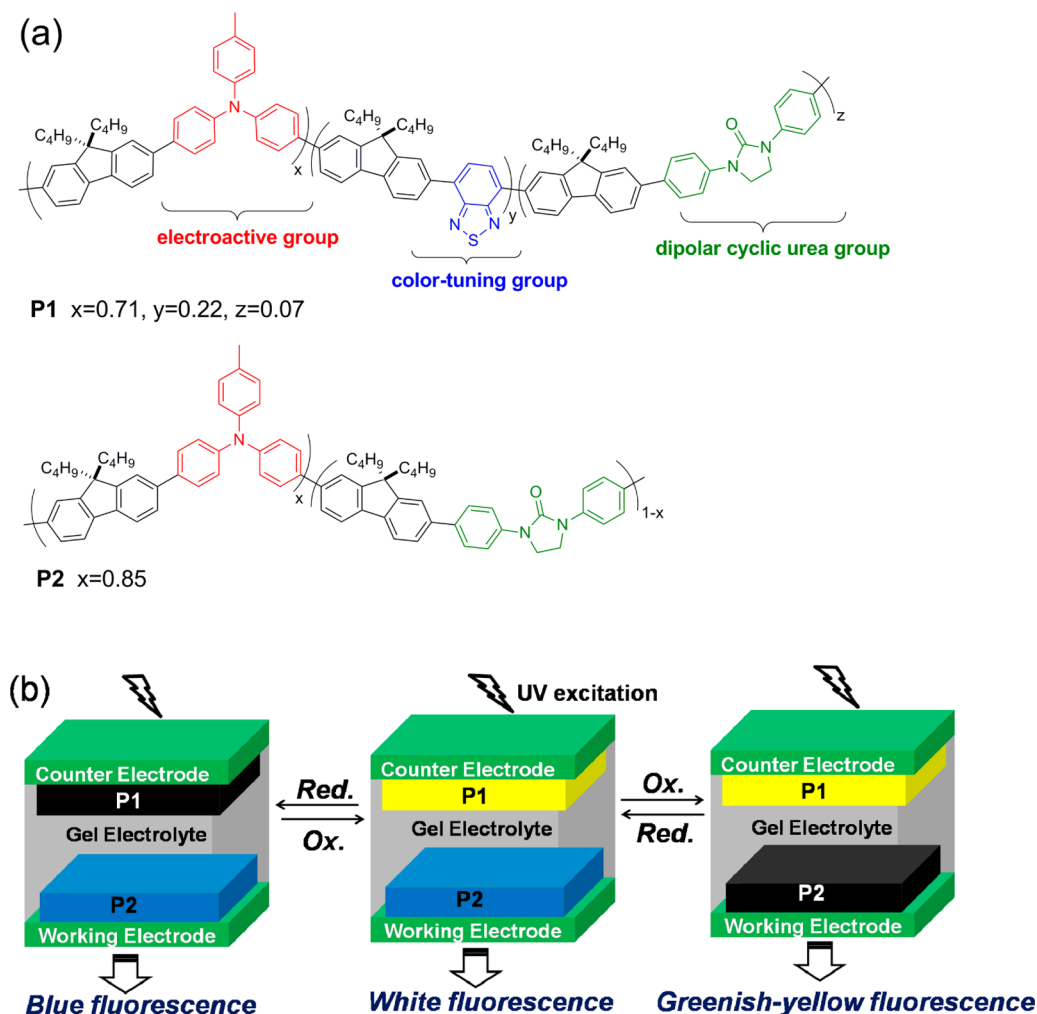
luminescence (PL) efficiency and excellent thermal stability in the solid state.[29−34] On the other hand, triarylamines (TAAs) are known to be oxidized easily to form stable radical cations, an effective quencher.[35−40] Incorporation of TAAs onto the fluorescent conjugated polymers as a switch becomes a useful idea for controlling EFCDs. Meanwhile, to benefit the ion transport during the electrochemical process and reduce the barrier of the triphenylamine radical cation formation, a dipolar cyclic urea moiety was also introduced into the polymer backbone.[20] In addition, a white-light emitting device in which the emission spectral range covers two complementary blue and yellow colors is achieved.[7] P1 has the color tuned through incorporation of the electron-deficient benzo[2,1,3]thiadiazole (BT) units[41−45] so that the emission could cover a wider range to greenish-yellow color spectral region. Therefore, the multicolor EFCD in which the white FL emission is composed of greenish-yellow FL from P1 and blue FL from P2, shows white-blue-(greenish-yellow) state of FL.

Different from Kim's device,[28] we suggest using oxidation of P1 and P2 as the fast fluorescent switching mechanisms. The ideas are shown in Scheme 1b; the device is fabricated with P1 and P2 that are coated individually on two complementary ITO electrodes. In this design, the light emitting behaviors of P1 and P2 will not be interfered by intermolecular energy transfer interactions. To form a complementary pair, the polymers have to fulfill several conditions: (1) The polymers have to be stable and reversible in the redox process under either the cathodic or the anodic processes. (2) The FL emission intensity should be maintained upon applying a negative bias. (3) To achieve a fast response device, the barriers for the ion diffusion should be low. Since the emissive states could be completely quenched by selectively controlling the EPs, we can successfully demonstrate, to our knowledge for the first time, a true blue-white-(greenish-yellow) EFCD under appropriate working conditions. The experimental results are discussed in the latter sections.

■ RESULTS AND DISCUSSION

Electrochemical Properties and EFC Switching of P1 and P2 in EFCDs (Type I). The electrochemical properties of the polymer films coated on an ITO electrode were investigated by cyclic voltammetry (CV) in an electrolyte of tetrabutylammoniumperchlorate (TBAP)/MeCN (0.1 M), using Pt wire as the counter electrode and Ag/AgCl couple as the reference. The scan rate being adopted was 100 mV/s. The polymer film was prepared by spin coating a solution of copolymer (10 mg mL^{-1} in CHCl$_3$) on ITO-coated glass substrate and then dried in vacuum. When the CV scans were swept between 0.0 and 1.0 V, P1 and P2 showed a strong oxidation wave at the 0.86 V due to the TAA moieties oxidation to form cation radicals (Figure 1). This results imply that introduction of the BT units does not cause significant effects on the TAA oxidation.
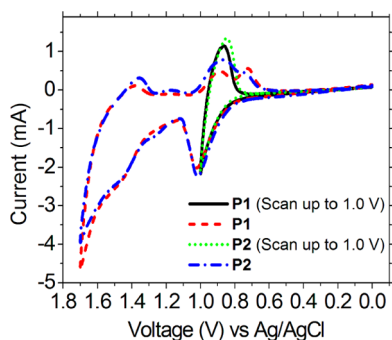
Figure 1. CV of the films of **P1** and **P2** on an ITO-coated glass substrate in TBAP/MeCN (0.1 M). The scan rate was 100 mV/s.

A traditional EFCD (Type I) is made of an emissive layer, with gel electrolyte being packed between the electrodes (Figure 2d). The EFCDs of **P1** and **P2** emit greenish-yellow and blue FL respectively. By comparing against the FL intensity of poly(9,9-dioctylfluorene) thin-film sample (Φ_{PL} = 0.55),[46] we estimated the PL quantum yields of **P1** and **P2** to be 0.23 and 0.74, respectively. By taking the advantage of the fast exciton migration properties of conjugated polymer films, only small amounts of quenchers are required to facilitate the fluorescence quenching phenomenon. Therefore, one may expect that the fluorescence switching phenomenon would occur in advance before +0.86 V. Indeed, upon application of positive potentials beyond +0.7 V, the fluorescence emission from the EFCD of **P1** was significantly quenched and became almost completely extinguished to dark after +1.0 V (Figure 2a). The FL quenching originates from the electrochemical oxidation of the triphenylamine units to form cation radicals. In addition, the EFCD of **P2** also shows similar oxidative FL quenching process (Figure 2b). On the other hand, when negative reverse bias EPs were applied to the films, the FL intensity can be resumed without causing any quenching phenomenon. The EFC switching mechanisms was elucidated

by spectroelectrochemistry. The oxidation process of **P1** in the EFCD was monitored (Figure 2c): Observation of the new absorption band at 500 nm at above +0.9 V, which is due to the triphenylamine radical cation absorption that covers the blue to yellow region, clearly supports our mechanistic hypothesis.[38]

To further understand the thin-film oxidation mechanisms, we adopted electrochemical quartz crystal microbalance (EQCM) technique as tool to trace the electrochemical process.[47] The QCM equips with a quartz crystal oscillating at a particular resonant frequency. Deposition of organic film, with mass change (Δm), on the crystal causes a decrease in the resonant frequency. The mass change (Δm) could therefore be measured by using this oscillating quartz crystal mass-sensing method with high precision. The EQCM technique integrates the quartz crystal balance into an electrochemical setup to monitor the mass changes directly at the electrode surface accompanying electrochemical processes. In the present experiments, **P1** and **P2** were respectively coated onto AT-cut quartz crystals with polished Pt electrode surfaces by drop-casting and drying of the polymer solution on top of the electrode. The effective Pt electrode surface area is 0.19 cm^2. A standard three-electrode configuration was employed for the EQCM experiments with the front electrode of the quartz crystal acting as the working electrode, Ag/AgCl electrode as the reference electrode, and a piece of Pt foil as the counter electrode. To mimic the EFCD conditions, LiClO$_4$ in propylene carbonate (PC, 0.1 M) was employed as the supporting electrolyte. As shown in Figure 3, an alternating step electrical potential sequence with the step potential increment of +0.1 V, starting from −1.0 V and gradually increasing to +1.0 V, was applied to the film. In both cases, the background resonance frequency slightly drifts to lower frequency below +0.8 V. The drift direction is mainly independent of the direction of the electrical potential bias. The background drift is due to the viscoelastic effects arising from the swelling phenomenon that refer to the change of the non/semirigid behavior of the deposited film on the quartz
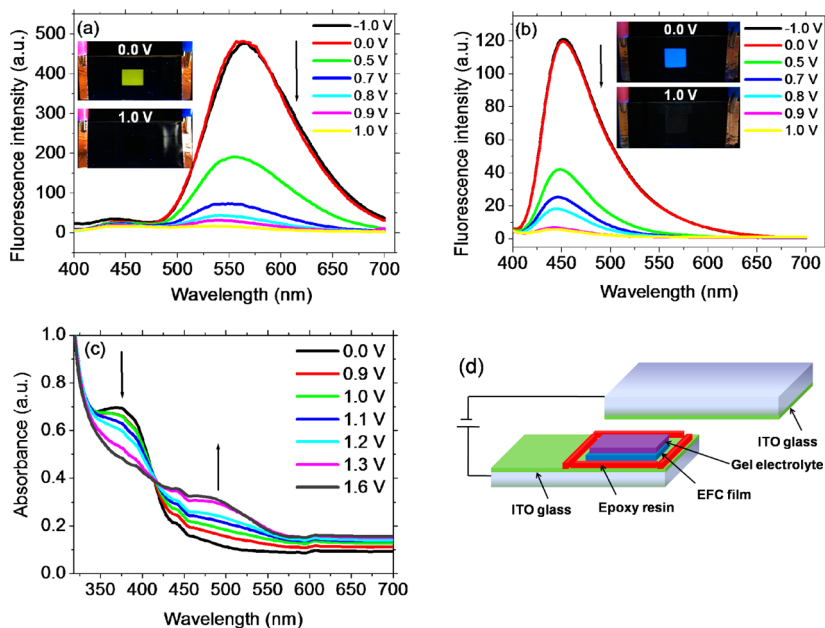

Figure 2. FL intensity changes (λ_{exc} = 380 nm) of EFCDs of (a) **P1** and (b) **P2** at different applied potentials. (c) Spectroelectrochemistry of the EFCD of **P1**. (d) Schematic diagram of the EFCD (Type I) sandwich cell.
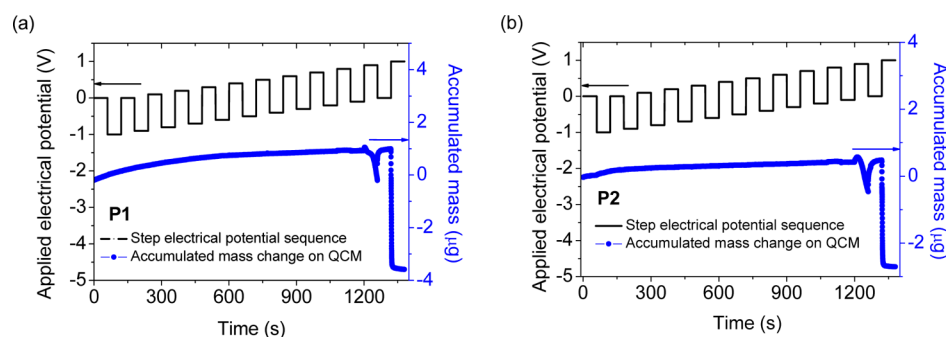
Figure 3. EQCM measurements for (a) **P1** and (b) **P2** on AT-cut quartz crystals with polished Pt electrode surfaces, using $LiClO_4$ in PC (0.1 M) as the supporting electrolyte. In the study, an alternating step electrical potential sequence with the step potential increment of +0.1 V and duration of 60 s was applied.

crystal. During the EQCM experiments, swelling of the solid polymer film may alter the effective mass of the film as well as the viscoelasticity that will alter the resonance frequency response of the system. On the other hand, when bias electrical potential of +0.9 V was applied to the film, noticeable change in the mass was observed. This process is reversible so that the resonance frequency could be resumed by reversal of the bias voltage. This might be due to the migration of Li^+ ions out of the matrix during film oxidation. Dramatic change of the mass was observed when the bias step-potential was switched to +1.0 V. In short summary, the above observations suggest that electrochemical oxidation of the film starts at around +0.8 to +0.9 V, which is consistent with our above observations and discussion. On the other hand, the films remain intact under the negative bias voltage conditions up to −1.0 V without causing any dramatic change in the mass. This result indicates that the films are inert toward electrochemical reduction but active toward electrochemical oxidation.

Although the BT units containing **P1** can be electrochemically reduced, the reduction potential range is not within our operation voltage region.[48] To further secure this point, we have applied up to −1.5 V to **P1** and concluded that the fluorescence properties (∼95%) mainly maintain. However, perhaps due to the low content of BT units in **P1**, no obvious reduction signal can be assigned in CV analysis upon using **P1** coated Pt plate as the working electrode

The FL switching responses of the solid-state EFCDs of **P1** and **P2** are as shown in Supporting Information (Figure S8). Redox pulse-cycles were carried out for the EFCDs of **P1** and **P2**. Fixed potential at 1.0 V (for oxidation) and at −1.0 V (for reduction) were used with a step duration time for 40, 30, 10, and 5 s at each potential. The EFC switching of **P1** and **P2** is highly reversible between a nonfluorescent monocation radical state at 1.0 V and a fluorescent neutral state at −1.0 V. The FL switching responses for the EFCD of **P1** were monitored at 560 nm and exhibited good switching performance of an on/off ratio of 23.8, maintaining a maximum on/off ratio of ≥15 for switching pulse times of 10 s and above (Table 1). However, with a faster switching pulse of 5 s, the on/off ratio decreased to

10.3, possibly due to a slow redox reaction for EFCD. In this experiment, the potential was quickly scanned without waiting for completion of the redox reaction of the triphenylamine units that the on/off ratio was therefore smaller than expected from the spectra changes in Figure 2a. On the other hand, the FL switching responses for the EFCD of **P2** were monitored at 450 nm and also showed good switching performance. On/off ratios of 21.9, 17.6, 11.3, and 8.7 were recorded with a step duration time for 40, 30, 10, and 5 s, respectively, at each potential (Table 1). Moreover, the switching time was estimated at 90% of the full switch. The EFCDs of **P1** and **P2** showed on-to-off switching times of 4.54 and 4.46 s at 1.0 V and off-to-on switching times of 5.62 and 4.33 s at −1.0 V, respectively.

Multicolor EFCD (Type II). The multicolor EFCD (Type II) contained two complementary electrodes of **P1** and **P2**. The gel electrolyte was sandwiched in between to form the device. The PL spectra of the EFCDs (Figure 4a), denoted respectively as EFCD-1, EFCD-1.2, EFCD-1.4, and EFCD-1.5, in which the number shown behind represents the thickness ratio of **P1** and **P2** (80 nm as a standard thickness) in the devices, showed the emission bands at 560 and 450 nm. The relative intensity varied when the thickness ratio of **P1** and **P2** was changed. Among them the EFCD-1.5 exhibited near white-light emission at the
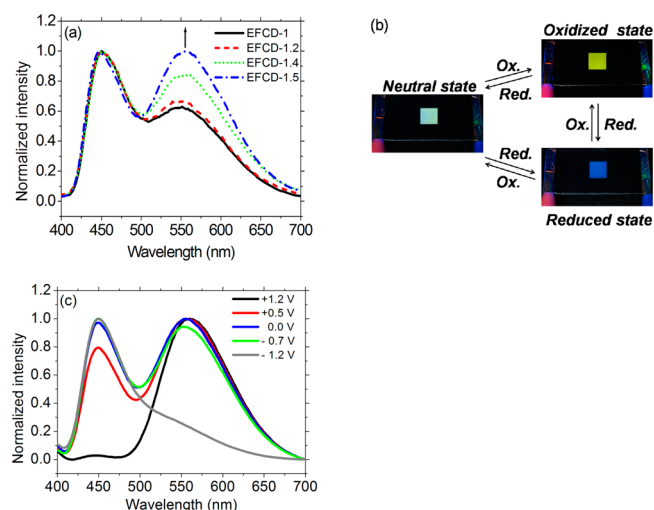

Figure 4. (a) PL spectra in EFCDs (λ_{exc} = 380 nm). (b) Photographs are the image of the FL changes of the EFCD-1.5 at indicated potentials under UV excitation (365 nm). (c) FL intensity changes (λ_{exc} = 380 nm) of EFCD-1.5 at different applied potentials.

Table 1. FL Switching Responses of EFCDs

EFCD	on/off ratio			
	40 s	30 s	10 s	5 s
P1	23.8	20.5	15.6	10.3
P2	21.9	17.6	11.3	8.7

1931 CIE coordinates of (0.31, 0.34). Due to the relatively large interfacial resistance of the polymer coated electrodes, higher operating electrical voltage ranged +1.2 V/−1.2 V is required to drive the EFCD.

FL intensity changes of the EFCD-1.5 upon increasing electrical voltage strongly support the hypothesis (Figure 4b, c). In the neutral state, the device of EFCD-1.5 emitted white light under UV irradiation. The blue component was selectively quenched by applied EP to P2. Under this circumstance, the greenish-yellow FL from P1 became dominant. The quenching process can be reversed so that the white light FL can be regenerated at neutral conditions. Similarly, the greenish-yellow emission can also be gradually suppressed by applying a reverse bias of electrical voltage to the P2 electrode to give blue FL. The quenching process of P2 in the EFCD-1.5 under oxidized state is demonstrated in Scheme 2. Under +1.2 V, P2 layer will

Scheme 2. Schematic Illustration Describes the Quenching Mechanism of P2 in the EFCD-1.5[a]
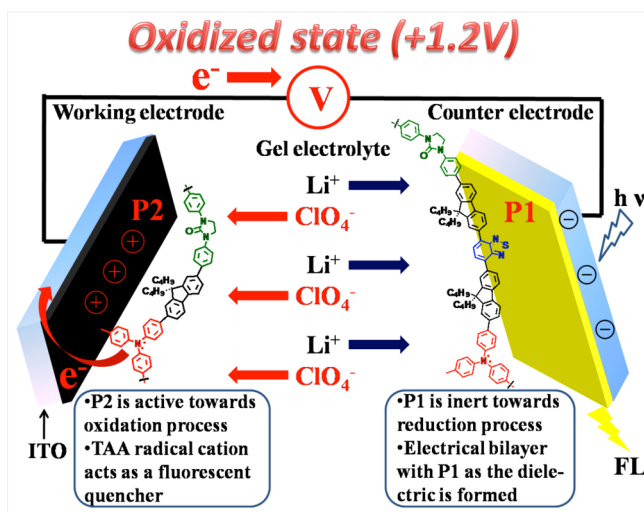
[a]When a forward bias voltage of +1.2 V is applied to P2, P2 will be partially oxidized on the anode and the fluorescent properties will be suppressed. Meanwhile ITO on the cathode will be reduced to form an electrical bilayer. P1 will act as dielectric for the bilayer.

be partially doped. Generation of TAA radicals in the P2 layer leads to effective quenching of the blue FL. Therefore, only the greenish-yellow FL could be observed.

Figure 5 shows the FL switching profile of EFCD-1.5 in a redox pulse-cycle. The FL switching response of EFCD-1.5 was monitored at 560 and 450 nm for P1 and P2, respectively. In these tests, the EP of the P2 electrode was flipped with respect to that of P1 with a step duration time of 30 s at each potential. Three different pulse sequences of (1) +1.2 and −1.2 V, (2) +1.2 and 0.0 V, and (3) −1.2 and 0.0 V were tested.

At the beginning of the first pulse-cycle, the EP of P2 was kept at +1.2 V with respect to P1. The FL of P2 was suppressed due to electrical oxidation so that only greenish-yellow FL at 560 nm was observed at this stage. When the potential of P2 was flipped to −1.2 V, the greenish-yellow FL (560 nm) was quenched with the blue FL (450 nm) arouse simultaneously. The FL emission could be reversed to the greenish-yellow once flipping the potential of P2 back to +1.2 V.

In the second pulse-cycle sequence, the EP of P2 was switched from +1.2 to 0.0 V instead of switched to −1.2 V. The
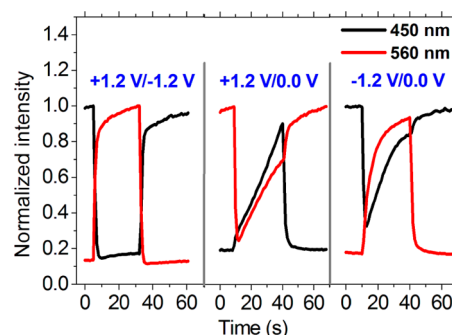

Figure 5. FL switching responses (λ_{exc} = 380 nm) of EFCD-1.5 between multicolor states with a step duration time for 30 s at each potential.

blue FL of P2 gradually resumed as expected but in a slower rate. On the other hand, the greenish-yellow FL intensity from P1 dropped simultaneously at first stage (Scheme 3). Therefore, the apparent device emission was changed from greenish-yellow to white. The FL intensity was much weaker than that of the original one at the beginning, indicating that both P1 and P2 are partially doped with TAA radical cations. The redistribution of the TAA radical cations proceeded quickly so that 90% of the FL intensity was diminished within 1.45 s. The P1 emission intensity bounced back along with increasing the blue FL of P2 at second stage. This indicated that the TAA radical cationic sites were gradually neutralized. The white emission intensity went back to 90% of the original emission strength within 28.7 s. The complementary FL switch from blue to white was also observed when a potential step function from −1.2 to 0.0 V was applied to the device.

A prototype of the multicolor EFCD is shown in Figure 6. The letters of E and F were written by spin-coating solution of P2 on the ITO electrode, over a stencil. On the other layer, the polymer film was deposited by spin-coating solution of P1 on the counter ITO electrode. In this EFCD, the letters of E and F show white emission under neutral state. When a voltage of +1.2 V was applied to P2, the EFCD completely displays greenish-yellow emission due to electrochemical oxidation for P2. Moreover, upon applied potential at −1.2 V, the letters of E and F exhibit blue emission because of electrochemical oxidation for P1.

The electrochemical process of the multicolor EFCD was further followed by CV methods, using Ag/AgCl couple as the internal reference. The active electrode surface area is 2.25 cm². Figure 7(a and b) shows the CV diagrams of the multicolor EFCD. In the experiment shown in Figure 7a, the P1 coated ITO was used as the working electrode while the P2 coated ITO was used as the counter electrode. On the other hand, in the experiment shown in Figure 7b, the P2 coated ITO was used as the working electrode. Figure 7c shows the CV of the multicolor EFCD that was scanned under the operation conditions, using a two-electrode configuration. These CV-plots are highly diagnostic of the redox process and are informative about the charge injection process.

Figure 7(a and b) show the anodic waves of P1 and P2 starting at 0.80 and 0.87 V, respectively, which is consistent with the results obtained from the EQCM studies. It is noteworthy to point out that the peak currents are around 1 mA scale. However, under the condition of EFCD operation in which the potential difference of P2 versus P1 is controlled, the current density reached the level of 10−20 μA at ±1.2 V. These

Scheme 3. Schematic Illustration of the Neutralization Process (+1.2 to 0.0 V) of P1 and P2 in an EFCD-1.5
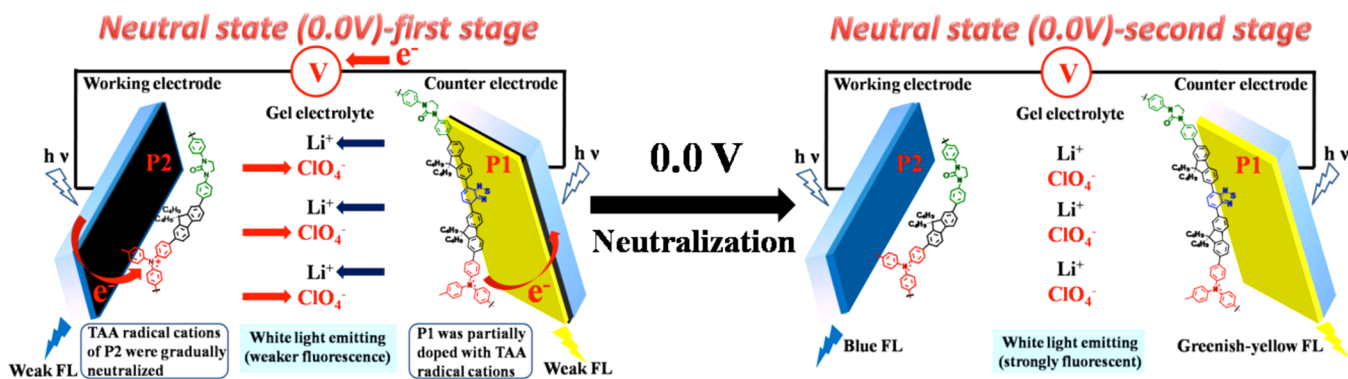

Figure 6. Photographs are the image of the reversible FL switching cell, at given potential.
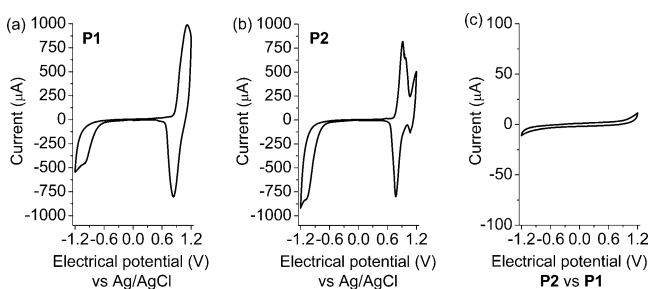

Figure 7. CV diagrams of the multicolor EFCD: (a) **P1** coated ITO was used as the working electrode; (b) **P2** coated ITO was used as the working electrode. (c) CV sweep of the multicolor EFCD, using a two-electrode configuration and under the operation conditions.

values are about 1% to 2% of the peak current obtained in the CV studies. The large current discrepancy suggests that the fluorescent switching process operates at the very earlier stage of the electrochemical oxidation. This is reasonable because, unlike traditional electrochromic devices that rely on high degree of redox change to obtain high on/off color-switching, efficient fluorescence quenching of the conjugated polymer due to fast exciton migration only requires small extents of redox change in the film in EFCD.[19]

One remaining puzzle to solve is that the potential difference of 1.2 V imposed between the two electrodes may not be high enough to perform two redox processes for the **P1/P2** couple. In particular, **P1** and **P2** show high stability against electrochemical reduction. However, Joseph and co-workers have reported that ITO undergoes substantial changes during cathodic polarization.[49] During cycling within the potential range from 0.0 to −1.2 V versus SCE, the reduction of Sn^{4+}, or In^{3+} in the ITO film to lower oxidation states occurs, leading to substantial changes in ITO. In Figure 7(a and b), one can see a reduction wave peaking at around −1.0 V, which is in good agreement with the reported observation about ITO under the almost neutral condition of pH 6.2. The ITO reduction assignment has been further confirmed by cathodic CV studies, using a piece of bare ITO electrode as the working electrode (Supporting Information Figure S11). This result indicates that ITO can act as an electrochemically active cathodic material.

CONCLUSIONS

In summary, we herein successfully demonstrated the multi-color EFCD based on a new concept of using oxidative switching fluorescent layers on both complementary electrodes. The multicolor EFCD was functioned through a reversibly switching mechanism among the zero-bias state (white emission), the positive bias state (greenish-yellow emission), and the negative bias state (blue emission) by complementary layers of **P1** and **P2**. Dependent on the doping level, the emission intensity from either **P1** or **P2** can be continuously tuned so that EFCD with different spectral properties can be achieved. The mechanistic study revealed that the fluorescence quenching process at the anode is controlled by triarylamine radical cations formation, which acts as effective fluorescent quenchers for fluorescence suppression. On the other hand, the ITO acts as the cathodic material and **P1** acts as a dielectric layer under the cathodic conditions (Scheme 2). Hence, electrical bilayer might form on the cathodic ITO electrode surface. Different from traditional electrochromic devices that usually require nearly stoichiometric conversion in order to facilitate high contrast chromic change, EFCDs only require low extents of charge injection into the polymer layer. Therefore, the cathodic ITO electrical bilayer formation on the electrode surface can be easily achieved.

ASSOCIATED CONTENT

⑤ Supporting Information

Full details on materials synthesis and fabrication of electro-fluorochromic devices. Figures showing UV−vis absorption and PL spectra of **P1** and **P2** in $CHCl_3$ solution and solid-film state. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors
*Email: mkleung@ntu.edu.tw.
*Email: kcho@ntu.edu.tw.

Notes
The authors declare no competing financial interest.

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■ REFERENCES

(1) Seo, S.; Pascal, S.; Park, C.; Shin, K.; Yang, X.; Maury, O.; Sarwade, B. D.; Andraud, C.; Kim, E. NIR Electrochemical Fluorescence Switching from Polymethine Dyes. *Chem. Sci.* **2014**, *5*, 1538−1544.

(2) Yen, H.-J.; Liou, G.-S. Flexible Electrofluorochromic Devices with the Highest Contrast Ratio Based on Aggregation-Enhanced Emission (AEE)-Active Cyanotriphenylamine-Based Polymers. *Chem. Commun.* **2013**, *49*, 9797−9799.

(3) Wang, B.; Bi, L.-H.; Wu, L.-X. Electroswitchable Fluorescent Thin Film Controlled by Polyoxometalate. *J. Mater. Chem.* **2011**, *21*, 69−71.

(4) Martínez, R.; Ratera, I.; Tárraga, A.; Molina, P.; Veciana, J. A Simple and Robust Reversible Redox-Fluorescence Molecular Switch Based on a 1,4-Disubstituted Azine with Ferrocene and Pyrene Units. *Chem. Commun.* **2006**, *36*, 3809−3811.

(5) Kim, Y.; Kim, E.; Clavier, G.; Audebert, P. New Tetrazine-Based Fluoroelectrochromic Window; Modulation of the Fluorescence Through Applied Potential. *Chem. Commun.* **2006**, *34*, 3612−3614.

(6) Seo, S.; Kim, Y.; You, J.; Sarwade, B. D.; Wadgaonkar, P. P.; Menon, S. K.; More, A. S.; Kim, E. Electrochemical Fluorescence Switching from a Patternable Poly(1,3,4-oxadiazole) Thin Film. *Macromol. Rapid Commun.* **2011**, *32*, 637−643.

(7) Seo, S.; Kim, Y.; Zhou, Q.; Clavier, G.; Audebert, P.; Kim, E. White Electrofluorescence Switching from Electrochemically Convertible Yellow Fluorescent Dyad. *Adv. Funct. Mater.* **2012**, *22*, 3556−3561.

(8) Miomandre, F.; Lépicier, E.; Munteanu, S.; Galangau, O.; Audibert, J. F.; Méallet-Renault, R.; Audebert, P.; Pansu, R. B. Electrochemical Monitoring of the Fluorescence Emission of Tetrazine and Bodipy Dyes Using Total Internal Reflection Fluorescence Microscopy Coupled to Electrochemistry. *ACS Appl. Mater. Interfaces* **2011**, *3*, 690−696.

(9) Audebert, P.; Miomandre, F. Electrofluorochromism: from Molecular Systems to Set-up and Display. *Chem. Sci.* **2013**, *4*, 575−584.

(10) Montilla, F.; Mallavia, R. On the Origin of Green Emission Bands in Fluorene-Based Conjugated Polymers. *Adv. Funct. Mater.* **2007**, *17*, 71−78.

(11) Montilla, F.; Frutos, L. M.; Mateo, C. R.; Mallavia, R. Fluorescence Emission Anisotropy Coupled to an Electrochemical System: Study of Exciton Dynamics in Conjugated Polymers. *J. Phys. Chem. C* **2007**, *111*, 18405−18410.

(12) Montilla, F.; Mallavia, R. In Situ Electrochemical Fluorescence Studies of PPV. *J. Phys. Chem. B* **2006**, *110*, 25791−25796.

(13) Nakamura, K.; Kanazawa, K.; Kobayashi, N. Electrochemically Controllable Emission and Coloration by Using Europium(III) Complex and Viologen Derivatives. *Chem. Commun.* **2011**, *47*, 10064−10066.

(14) Quinton, C.; Alain-Rizzo, V.; Dumas-Verdes, C.; Miomandre, F.; Audebert, P. Tetrazine−Triphenylamine Dyads: Influence of the Nature of the Linker on Their Properties. *Electrochim. Acta* **2013**, *110*, 693−701.

(15) Miomandre, F.; Audibert, J. F.; Zhou, Q.; Audebert, P.; Martin, P.; Lacroix, J. C. Electrochemically Monitored Fluorescence on Plasmonic Gratings: A First Step Toward Smart Displays with Multiple Inputs. *Electrochim. Acta* **2013**, *110*, 56−62.

(16) Quinton, C.; Alain-Rizzo, V.; Dumas-Verdes, C.; Clavier, G.; Miomandre, F.; Audebert, P. Design of New Tetrazine−Triphenyl-amine Bichromophores— Fluorescent Switching by Chemical Oxidation. *Eur. J. Org. Chem.* **2012**, *7*, 1394−1403.

(17) Swager, T. M. The Molecular Wire Approach to Sensory Signal Amplification. *Acc. Chem. Res.* **1998**, *31*, 201−207.

(18) Yang, J.-S.; Swager, T. M. Porous Shape Persistent Fluorescent Polymer Films: An Approach to TNT Sensory Materials. *J. Am. Chem. Soc.* **1998**, *120*, 5321−5322.

(19) Zhou, Q.; Swager, T. M. Method for Enhancing the Sensitivity of Fluorescent Chemosensors: Energy Migration in Conjugated Polymers. *J. Am. Chem. Soc.* **1995**, *117*, 7017−7018.

(20) Kuo, C.-P.; Lin, Y.-S.; Leung, M.-k. Electrochemical Fluorescence Switching Properties of Conjugated Polymers Composed of Triphenylamine, Fluorene, and Cyclic Urea Moieties. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 5068−5078.

(21) Kuo, C.-P.; Chuang, C.-N.; Chang, C.-L.; Leung, M.-k.; Lian, H.-Y.; Wu, K. C.-W. White-Light Electrofluorescence Switching from Electrochemically Convertible Yellow and Blue Fluorescent Conjugated Polymers. *J. Mater. Chem. C* **2013**, *1*, 2121−2130.

(22) Shen, K.-Y.; Hu, C.-W.; Chang, L.-C.; Ho, K.-C. A Complementary Electrochromic Device Based on Carbon Nanotubes/Conducting Polymers. *Sol. Energy Mater. Sol. Cells* **2012**, *98*, 294−299.

(23) Leventis, N.; Chung, Y. C. New Complementary Electrochromic System Based on Poly(pyrrole)-Prussian Blue Composite, a Benzylviologen Polymer, and Poly(vinylpyrrolidone)/Potassium Sulfate Aqueous Electrolyte. *Chem. Mater.* **1992**, *4*, 1415−1422.

(24) DeLongchamp, D.; Hammond, P. T. Layer-by-Layer Assembly of PEDOT/Polyaniline Electrochromic Devices. *Adv. Mater.* **2001**, *13*, 1455−1459.

(25) Cutler, C. A.; Bouguettaya, M.; Reynolds, J. R. PEDOT Polyelectrolyte Based Electrochromic Films via Electrostatic Adsorption. *Adv. Mater.* **2002**, *14*, 684−688.

(26) Schwendeman, I.; Hickman, R.; Sönmez, G.; Schottland, P.; Zong, K.; Welsh, D. M.; Reynolds, J. R. Enhanced Contrast Dual Polymer Electrochromic Devices. *Chem. Mater.* **2002**, *14*, 3118−3122.

(27) Rauh, R. D.; Wang, F.; Reynolds, J. R.; Meeker, D. L. High Coloration Efficiency Electrochromics and Their Application to Multi-Color Devices. *Electrochim. Acta* **2001**, *46*, 2023−2029.

(28) Seo, S.; Park, C.; Yang, X.; You, J.; Kim, Y.; Kim, E. Reversible Multi-Color Electrofluorescence Switching. *Proc. SPIE* **2012**, 82580N−82580N-6.

(29) Scherf, U.; List, E. J. W. Semiconducting Polyfluorenes— Towards Reliable Structure−Property Relationships. *Adv. Mater.* **2002**, *14*, 477−487.

(30) Chen, L.; Li, P.; Tong, H.; Xie, Z.; Wang, L.; Jing, X.; Wang, F. White Electroluminescent Single-Polymer Achieved by Incorporating Three Polyfluorene Blue Arms Into a Star-Shaped Orange Core. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 2854−2862.

(31) Shih, H.-M.; Wu, R.-C.; Shih, P.-I.; Wang, C.-L.; Hsu, C.-S. Synthesis of Fluorene-Based Hyperbranched Polymers for Solution-Processable Blue, Green, Red, and White Light-Emitting Devices. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 696−710.

(32) Tan, H.; Yu, J.; Wang, Y.; Li, J.; Cui, J.; Luo, J.; Shi, D.; Chen, K.; Liu, Y.; Nie, K.; Zhu, W. Improving Optoelectronic Properties of the 2,7-Polyfluorene Derivatives with Carbazole and Oxadiazole Pendants by Incorporating the Blue-Emitting Iridium Complex Pendants in C-9 Position of Fluorine Unit. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 149−155.

(33) Shu, C.-F.; Dodda, R.; Wu, F.-I.; Liu, M. S.; Jen, A. K. Y. Highly Efficient Blue-Light-Emitting Diodes from Polyfluorene Containing Bipolar Pendant Groups. *Macromolecules* **2003**, *36*, 6698−6703.

(34) Li, Y.; Ding, J.; Day, M.; Tao, Y.; Lu, J.; D'Iorio, M. Synthesis and Properties of Random and Alternating Fluorene/Carbazole Copolymers for Use in Blue Light-Emitting Devices. *Chem. Mater.* **2004**, *16*, 2165−2173.

(35) Yu, W.-L.; Pei, J.; Huang, W.; Heeger, A. J. A Novel Triarylamine-Based Conjugated Polymer and Its Unusual Light-Emitting Properties. *Chem. Commun.* **2000**, *36*, 681−682.

(36) Wang, H.-M.; Hsiao, S.-H. Enhanced Redox Stability and Electrochromic Properties of Aromatic Polyamides Based on N,N-bis(4-carboxyphenyl)-N′,N′-bis(4-tert-butylphenyl)-1,4-phenylenediamine. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 337−351.

(37) Li, Y.; Michinobu, T. Click Synthesis and Reversible Electrochromic Behaviors of Novel Polystyrenes Bearing Aromatic Amine Units. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 2111−2120.

(38) Chou, M.-Y.; Leung, M.-k.; Su, Y. O.; Chiang, C. L.; Lin, C.-C.; Liu, J.-H.; Kuo, C.-K.; Mou, C.-Y. Electropolymerization of Starburst Triarylamines and Their Application to Electrochromism and Electroluminescence. *Chem. Mater.* **2004**, *16*, 654−661.

(39) Cheng, S.-H.; Hsiao, S.-H.; Su, T.-H.; Liou, G.-S. Novel Aromatic Poly(Amine-Imide)s Bearing A Pendent Triphenylamine Group: Synthesis, Thermal, Photophysical, Electrochemical, and Electrochromic Characteristics. *Macromolecules* **2004**, *38*, 307−316.

(40) Liou, G.-S.; Hsiao, S.-H.; Huang, N.-K.; Yang, Y.-L. Synthesis, Photophysical, and Electrochromic Characterization of Wholly Aromatic Polyamide Blue-Light-Emitting Materials. *Macromolecules* **2006**, *39*, 5337−5346.

(41) Millard, I. S. High-Efficiency Polyfluorene Polymers Suitable for RGB Applications. *Synth. Met.* **2000**, *111−112*, 119−123.

(42) Müller, C. D.; Falcou, A.; Reckefuss, N.; Rojahn, M.; Wiederhirn, V.; Rudati, P.; Frohne, H.; Nuyken, O.; Becker, H.; Meerholz, K. Multicolor Organic Light-Emitting Displays by Solution Processing. *Nature* **2003**, *421*, 829−833.

(43) Justin Thomas, K. R.; Lin, J. T.; Velusamy, M.; Tao, Y.-T.; Chuen, C.-H. Color Tuning in Benzo[1,2,5]thiadiazole-Based Small Molecules by Amino Conjugation/Deconjugation: Bright Red-Light-Emitting Diodes. *Adv. Funct. Mater.* **2004**, *14*, 83−90.

(44) Liu, J.; Bu, L.; Dong, J.; Zhou, Q.; Geng, Y.; Ma, D.; Wang, L.; Jing, X.; Wang, F. Green Light-Emitting Polyfluorenes with Improved Color Purity Incorporated with 4,7-Diphenyl-2,1,3-benzothiadiazole Moieties. *J. Mater. Chem.* **2007**, *17*, 2832−2838.

(45) Omer, K. M.; Ku, S.-Y.; Wong, K.-T.; Bard, A. J. Green Electrogenerated Chemiluminescence of Highly Fluorescent Benzothiadiazole and Fluorene Derivatives. *J. Am. Chem. Soc.* **2009**, *131*, 10733−10741.

(46) Su, H.-J.; Wu, F.-I.; Tseng, Y.-H.; Shu, C.-F. Color Tuning of a Light-Emitting Polymer: Polyfluorene-Containing Pendant Amino-Substituted Distyrylarylene Units. *Adv. Funct. Mater.* **2005**, *15*, 1209−1216.

(47) Buttry, D. A.; Ward, M. D. Measurement of Interfacial Processes at Electrode Surfaces with the Electrochemical Quartz Crystal Microbalance. *Chem. Rev.* **1992**, *92*, 1355−1379.

(48) Wen, S.; Pei, J.; Zhou, Y.; Li, P.; Xue, L.; Li, Y.; Xu, B.; Tian, W. Synthesis of 4,7-Diphenyl-2,1,3-Benzothiadiazole-Based Copolymers and Their Photovoltaic Applications. *Macromolecules* **2009**, *42*, 4977−4984.

(49) Senthilkumara, M.; Mathiyarasu, J.; Joseph, J.; Phani, K. L. N.; Yegnaraman, V. Electrochemical Instability of Indium Tin Oxide (ITO) Glass in Acidic pH Range During Cathodic Polarization. *Mater. Chem. Phys.* **2008**, *108*, 403−407.