

High-performance fluorescent/electroactive polyamide bearing *p*-phenylene diamine and asymmetrical SBF/TPA-based units for electrochromic and electrofluorochromic multifunctional applications

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Abstract Electrofluorochromic (EFC) materials with excellent comprehensive properties possess promising application prospect in optoelectronic and biological fields. Here, we report a novel and high-performance polyamide (SBF-HPA) containing stable electroactive *p*-phenylenediamine and asymmetrical spirobifluorene/triphenylamine-based groups acting as intrinsically electroactive fluorophore. The resulting polyamide showed high blue fluorescence with the quantum yield up to 69.7% and 9.4% for its solution and solid-film states, respectively. CV curves revealed two redox couples accompanied with two-stage color changes (near colorless-green-blue). Furthermore, the fluorescent/electroactive polyamide film exhibited an interesting EFC behavior integrated with superior cycling stability, high fluorescence contrast and fast on/off switching time, facilitating real-life applications in the near future.

1. INTRODUCTION

Electrofluorochromism, dealing with the reversible modulation of fluorescent intensity or color induced by electricity stimulus, is developing rapidly and intensively due to its extensive application foreground in optical displays, sensors, information encryption and fluorescence imaging.¹⁻³ The conversion of electrical signal to fluorescence signal reveals in-depth information of electrochemical and photophysical properties. In general, electrofluorochromic (EFC) materials can be classified into two categories. One is dyads or triads based on the mechanism of electron or energy transfer between a redox-active moiety and a luminophore,⁴⁻⁶ and the other is intrinsically electroactive fluorophores,⁷⁻¹⁰ which attract particular attention since their fluorescence can be simply and directly switched by electrochemically controlled redox reactions. To meet the need of real-life applications, the performances of switchable fluorophores including long-term stability, high contrast ratio and rapid response speed are all crucial. Besides, the facile processibility and excellent environment-resistance are also important to promote the commercialization. Therefore, the fluorescent/electroactive polymers will be the promising candidates. Although much effort has been devoted to optimize the EFC performances, few existing materials could integrate all the demand mentioned above. Exploration of novel EFC materials with superior comprehensive performances as well as their structure-property relationships is still much meaningful to promote the further applications of EFC devices. In this paper, we herein design and report a novel fluorescent/electroactive polyamide with *p*-phenylenediamine and asymmetrical SBF/TPA-based groups, aiming for simultaneous realization of high fluorescence contrast, high cycling stability, rapid switching speed and facile processibility. The intense electron coupling of the two nitrogen atoms in *p*-phenylenediamine could surely reduce the oxidation potential and increase the electrochemical stability. The asymmetrical SBF/TPA-based unit is expected to improve the solubility, solid-state fluorescence as well as response time resulting from the reduced close packing of polymer chains. The design strategy of the polyamide (SBF-HPA) is concluded in Figure 1.

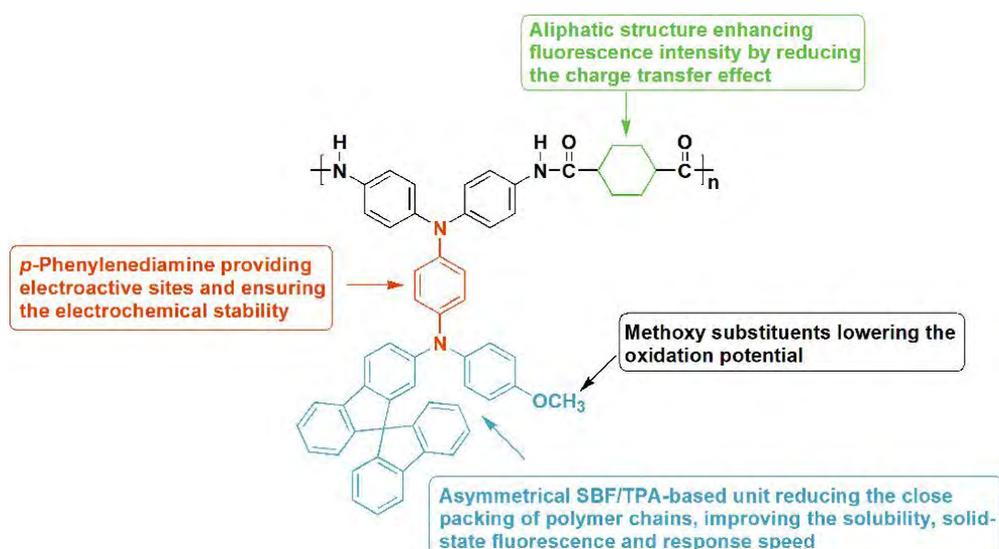


Figure 1. The design strategy of the polyamide (SBF-HPA) as high-performance EC and EFC dual-switching material.

2. EXPERIMENTAL

A novel diamine (SBF-2NH₂) bearing *p*-phenylenediamine and asymmetrical SBF/TPA-based groups was synthesized by a five-step route using the well-known and simple reactions of nucleophilic substitution, Ullmann and Pd/C-catalyzed hydrazine reduction as outlined in Scheme 1. Additionally, the polyamide SBF-HPA derived from the SBF-2NH₂ and *trans*-1,4-cyclohexanedicarboxylic acid was prepared through the phosphorylation technique (Scheme 2).

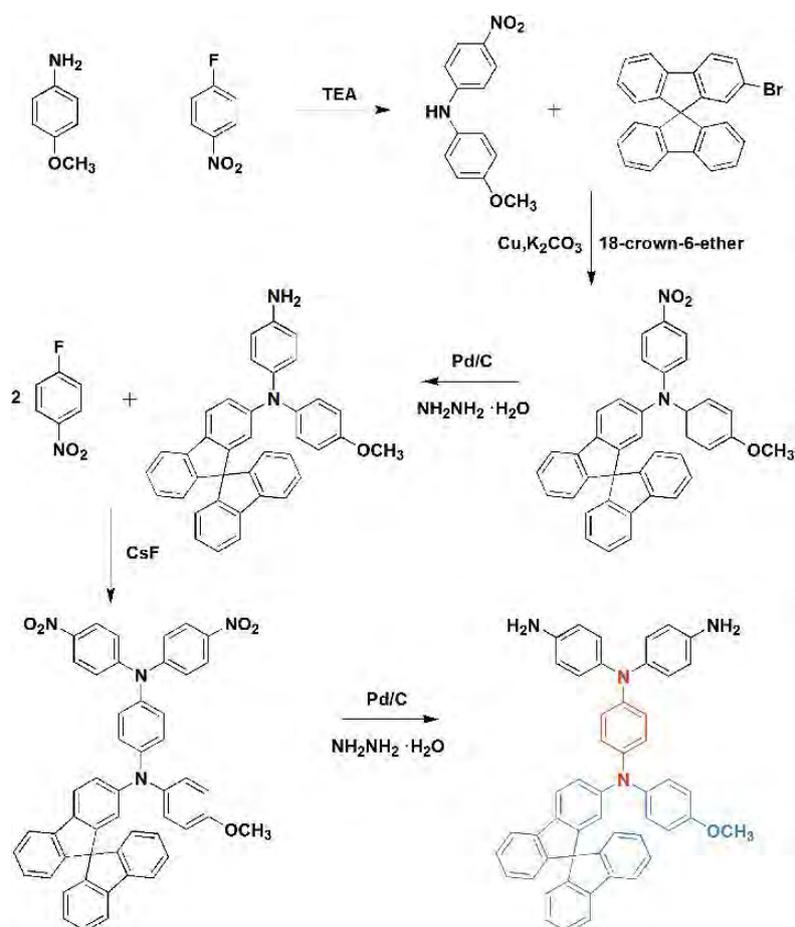
3. RESULTS AND DISCUSSION

Characterization

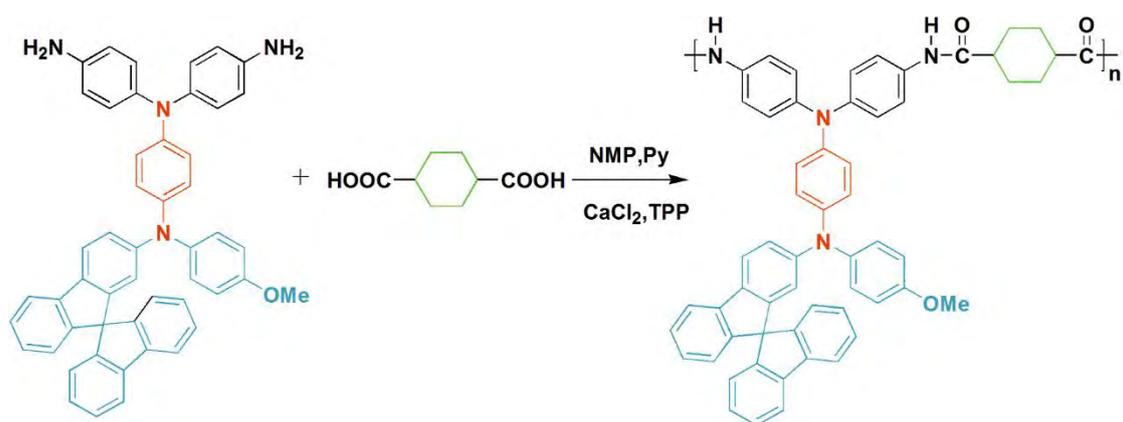
The structures of compound SBF-2NH₂ and the polyamide SBF-HPA were analyzed and verified through NMR measurements (Figure 2 and Figure 3).

Electrochemical properties

Cyclic voltammetry (CV) was performed to evaluate the electroactivity of the polyamide in a three-electrode electrochemical cell. As shown in Figure 4a, the SBF-HPA presented a typical CV scanning curves with two quasi-reversible one-electron redox peaks at 0.68/0.37 V and 1.07/0.72 V. The onset oxidation potential was found to be 0.37 V for SBF-HPA, by which the HOMO level was estimated to be 1.74 with ferrocene/ferrocenium (Fc/Fc⁺) as the standard (4.8 eV below vacuum). Notably, the SBF-HPA exhibited excellent reversibility for continuous 200 cyclic scans in the first redox stage (Figure 4b), which is much beneficial as an electro-tuner in the electroswitching systems. The fairly low onset oxidation potentials and extraordinary stability of mono-cation radical attributed to the structure of *p*-phenylenediamine were responsible for this highly stable electrochemistry properties.



Scheme 1. Synthetic route of SBF-2NH₂.



Scheme 2. Synthetic route of SBF-HPA.

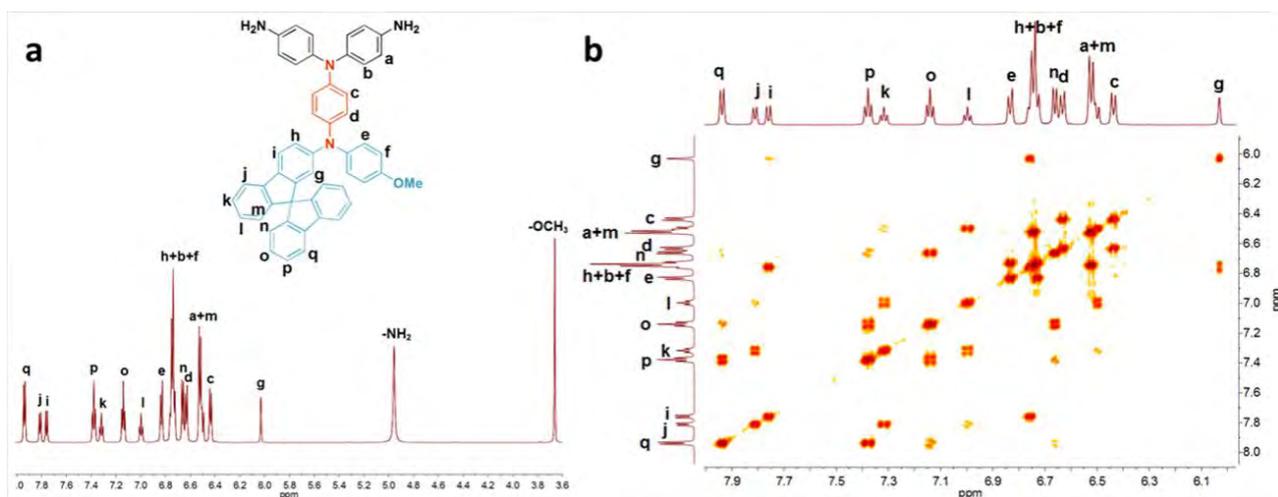


Figure 2. ^1H NMR (a) and H-H COSY (b) spectra of SBF-2NH₂.

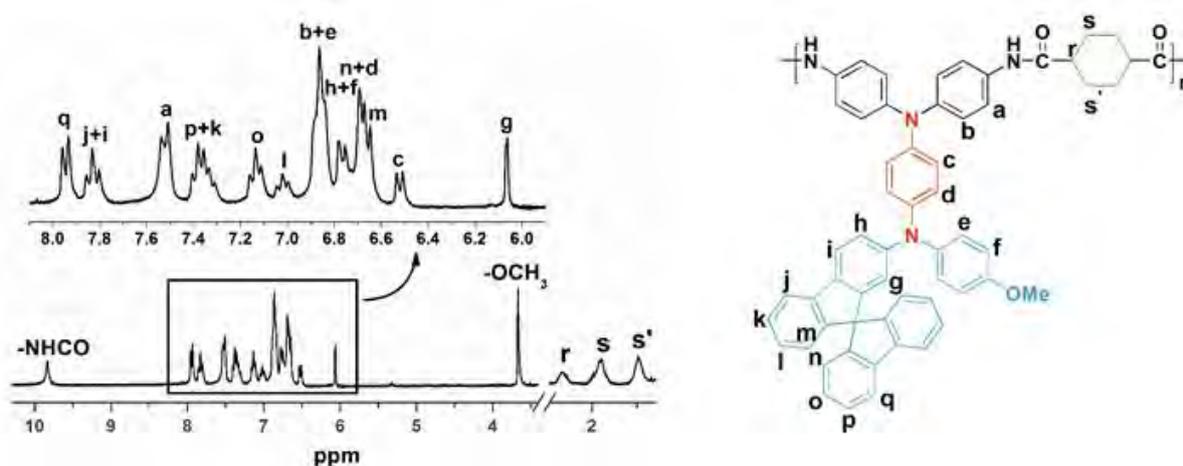


Figure 3. ^1H NMR spectra of SBF-HPA.

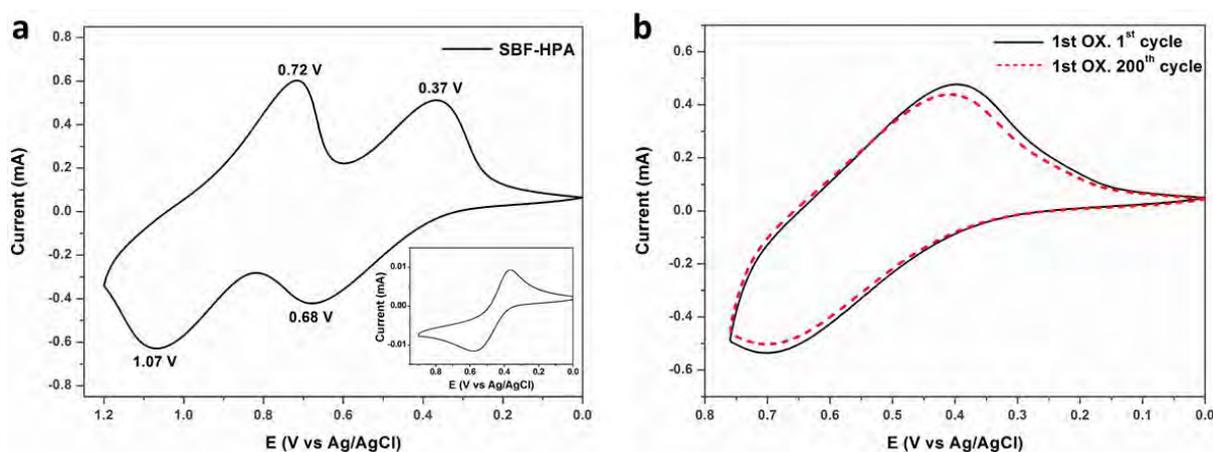


Figure 4. (a) CV diagrams of SBF-HPA at a scan rate of 50 mV s^{-1} . (b) CV diagrams of SBF-HPA for 200 cyclic scans in the first redox process at a scan rate of 50 mV s^{-1} .

Spectroelectrochemistry and electrochromic switching kinetics

We researched its spectroelectrochemistry by coupling the electrochemical workstation with UV-vis-NIR absorption spectra (Figure 5). As shown in Figure 5a, the SBF-HPA film revealed a characteristic absorption peak of 330 nm and the slight tail absorption around 400 nm at the neutral state of 0.00 V, which made it

almost transparent and colorless. Upon increasing the applied voltage from 0.00 to 0.80 V, the intensity of 330 nm absorption peak decreased gradually, while three new peaks at 430, 635 nm (visible-light region) and 1115 nm (NIR region) emerged. With the further oxidation from mono-cation radical to dication (applying voltage from 0.80 V to 1.15 V), the absorption peak of 430 nm and 1115 nm decreased while a new peak around 850 nm grew up. During this process, the SBF-HPA film realized triple color modulation from near colorless neutral state (CIE Yxy: 97.56, 0.3053, 0.3139) to green firstoxidized state (CIE Yxy: 44.77, 0.3131, 0.4257), and then to blue secondoxidized state (CIE Yxy: 30.74, 0.1970, 0.2433) (Figure 5b).

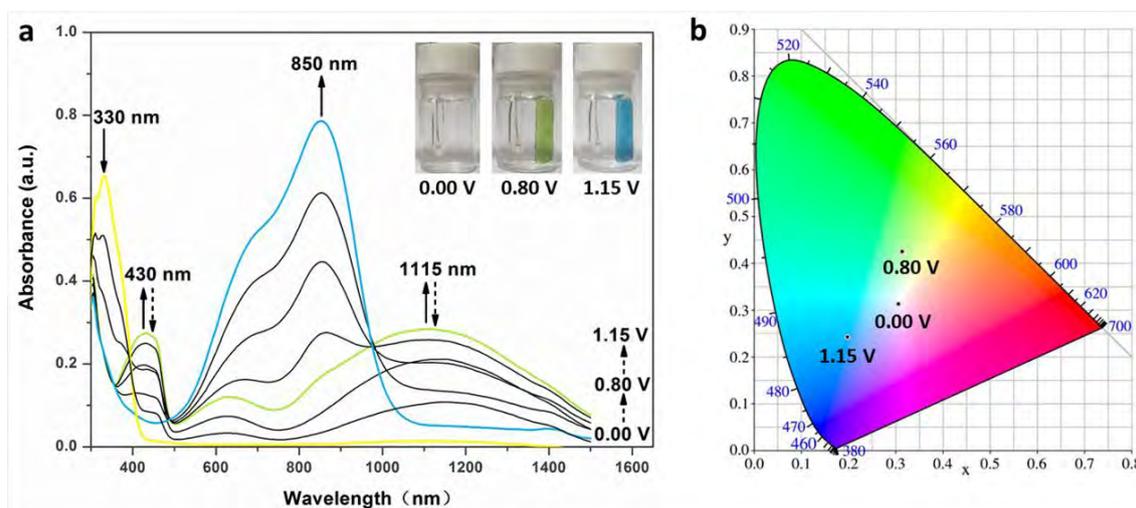


Figure 5. (a) Absorbance spectra of SBF-HPA thin film electrode in 0.1 M TBAP/CH₃CN at different applied potentials from 0.00 to 1.15 V. (b) CIE chromaticity of SBF-HPA thin film at different potentials (0.00 V Yxy: 97.56, 0.3053, 0.3139; 0.80 V Yxy: 44.77, 0.3131, 0.4257; 1.15 V Yxy: 30.74, 0.1970, 0.2433).

Furthermore, dynamic EC switching behaviors were also studied with the change of characteristic transmittance as a function of time by applying squarewave potential between neutral and oxidation states. Figure 6 depicted the first oxidation stage switching behaviors of SBF-HPA film between 0.00 and 0.80 V. As shown in Figure 6A, the optical contrast was found up to 65%, indicating a high optical modulation and obvious color changes. After 200 continuous cycles with a cycling time of 20 s, no evident decay of optical contrast could be seen, which demonstrated a high EC switching stability benefiting from the excellent electrochemical properties as mentioned above. Additionally, response time is also a crucial parameter to evaluate the performance of electrochromic materials, and here it was defined while attaining 90% of the total transmittance change. As shown in Figure 6B, the rapid response time of 2.3 s and 1.6 s in the coloring and blending process was ascribed to the loose packing resulting from the asymmetrical SBF/TPA-based group, which facilitated the insertion/extraction of electrolyte anion. When the potentials were switched between 0.00 and 1.15 V for the second oxidation stage switching behaviors of SBF-HPA (Figure 7), the film exhibited 1.9 s/3.2 s for coloration/bleaching and the optical contrast was calculated to be as high as 85%. On the basis of the switching studies, the coloration efficiency (CE) was estimated to be 246 cm²/C at 430 nm and 127 cm²/C at 850 nm through the following equation: $CE = \log(T_{\text{bleached}}/T_{\text{colored}})/Q_d$ (Q_d = injected/ejected charge during a redox step). The high CE value indicated that a small charge injection could lead to the great optical modulation, which will be energy-efficient for smart windows. Hence, the polyamide exhibited glorious electrochromic properties and may endow it with a promising applications in the field of displays, anti-glare rear-view mirrors and smart windows.

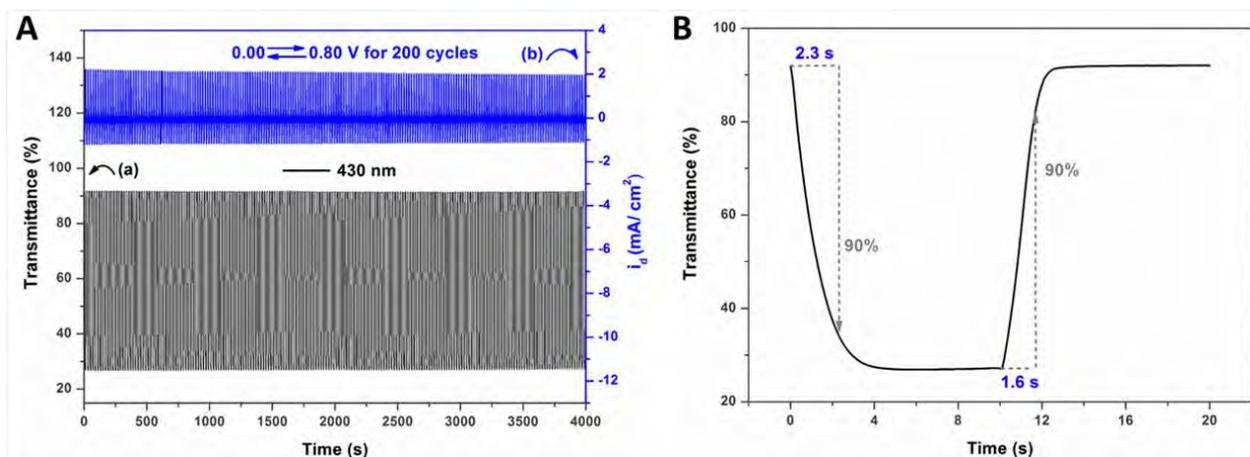


Figure 6. (A) EC switching of SBF-HPA film between 0.00 and 0.80 V with a cycle time of 20 s: (a) transmittance changes and (b) current consumption at the monitored wavelength of 430 nm. (B) Optical switching time at 430 nm.

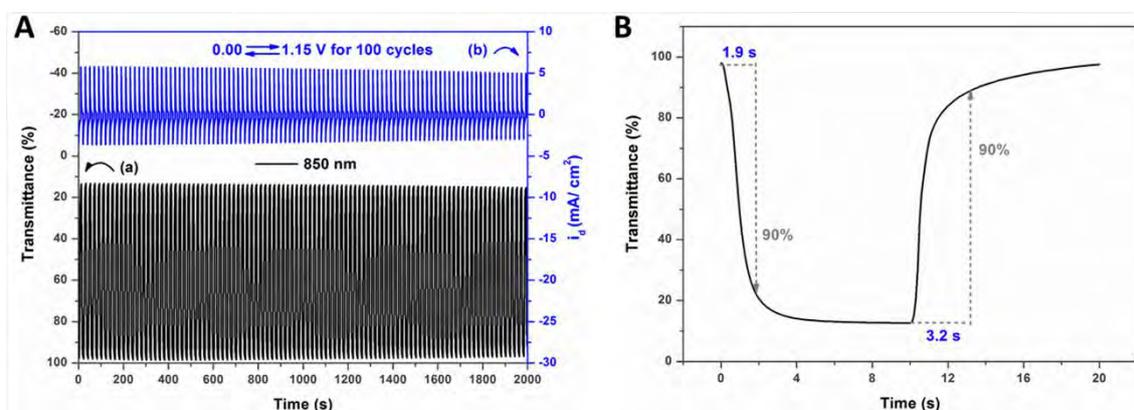


Figure 7. (A) EC switching of SBF-HPA film between 0.00 and 1.15 V with a cycle time of 20 s: (a) transmittance changes and (b) current consumption at the monitored wavelength of 850 nm. (B) Optical switching time at 850 nm.

EFC Property

Considering the high fluorescence intensity of SBF-HPA film and the effective quencher essence of TPA cation radical, the electrofluorochromism was recorded to quantify its potential-dependent emitting properties. As it can be seen in Figure 8A, the film exhibited glaring blue fluorescence in the neutral state. Upon increasing the potential from 0.0 to 0.7 V, the emission at 472 nm was gradually weakened, finally quenched. During the process, no shift of spectra band was observed suggesting that no side-reactions occurred. When applying the reverse potential to 0.0 V, the blue fluorescence could be recovered, indicating a reversible EFC behavior.

To further research the EFC performance, the response of EFC switching was monitored at the emission peak of 472 nm as a function of time by applying alternating voltage pulses from 0.0 to 0.7 V. In the first few cycles, the fluorescence intensity of neutral state and the quenching degree of oxidation state were diminished a little simultaneously owing to the inevitable charge trapping or some defect of the polyamide film and then keeping constant. Therefore, all the switching data were recorded after the film remained a steady state. Figure 8B revealed fluorescence switching response at different step duration time from 60 s to 10 s, indicating that the fluorescence contrast decreased concomitantly with reduced time, which can be explained by the incomplete redox at the short duration time. Meanwhile, the response time, defined as the time of 90% conversion, increased with the longer duration time. To simultaneously acquire high contrast and quick response time, the duration time of 20 s was an optimized choice with fluorescence contrast found up to 67 and on/off switching time calculated to be 2.3/0.3 s (Figure 8C). The high contrast ratio and rapid

response speed could be ascribed to the reduced interchain packing effect of asymmetrical group with bulky-twisted SBF, enhancing solid-state fluorescence intensity and accelerating the ions transport. For achieving real-life applications, the long-term stability of EFC behavior was also one of the most vital parameters. As shown in Figure 8D, the SBF-HPA exhibited extremely superior durability with no degradation observed after 200 cycles, benefiting from the highly electroactive stability of the *p*-phenylenediamine mentioned above. Hence, the SBF-HPA integrated with stable fluorescence switching, fast response speed and high fluorescence on/off contrast will greatly promote the practical applications of EFC materials in the near future.

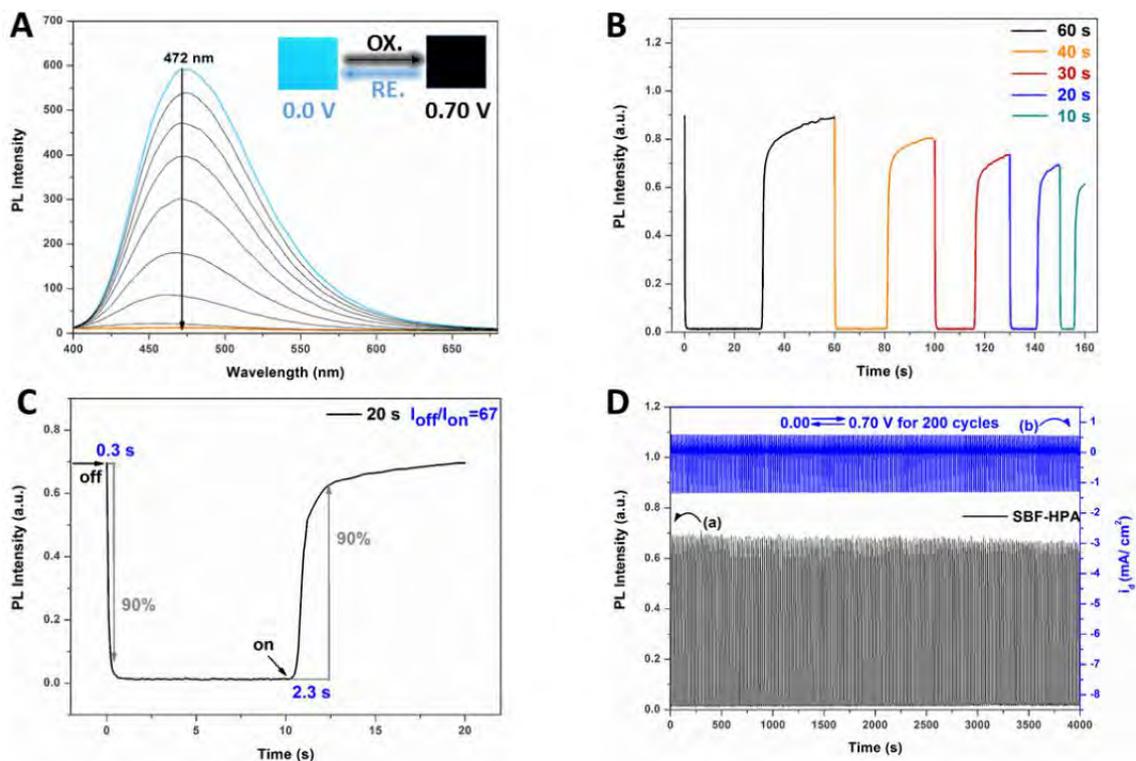


Figure 8. (A) PL spectra changes of SBF-HPA thin film electrode at different potentials under excitation at 350 nm (inset showed the optical images of polymer film under excitation of 365 nm with applied potential of 0.0 and 0.7 V, respectively). (B) EFC switching of SBF-HPA thin film electrode under applied potentials between 0.0 V and 0.7 V with duration time set as 60 s, 40 s, 30 s, 20 s, 10 s. (C) Optical switching time with a cycle time of 20 s. (D) EFC switching of SBF-HPA thin film electrode under applied potentials between 0.0 and 0.7 V with a cycle time of 20 s: (a) fluorescence intensity changes and (b) current consumption (monitored at 472 nm).

4. CONCLUSION

In summary, a novel electroactive polyamide SBF-HPA was designed and prepared by the construction of an intrinsically switching fluorophore based on *p*-phenylenediamine and asymmetrical SBF/TPA-based groups. The feature structure could effectively insure the stability of TPA mono-cation radical and reduce the interchain packing. Consequently, the SBF-HPA integrated with excellent solubility, thermal stability, high electrochemistry stability, fast response speed, high fluorescence contrast and highly stable EC/EFC switching over 200 cycles. Overall, this study not only supplies a new design concept for the high-performance fluorescent/electroactive materials, but also paves the way for their smart applications in the future.

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