

Simultaneously Achieving High Capacity Storage and Multilevel Anti-Counterfeiting Using Electrochromic and Electrofluorochromic Dual-Functional AIE Polymers

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ABSTRACT: With the advent of the big data era, information storage and security are becoming increasingly important. However, high capacity information storage and multilevel anti-counterfeiting are typically difficult to simultaneously achieve. To address this challenge, herein, two electrochromic and electrofluorochromic dual-functional polymers with aggregation-induced emission (AIE) features are skillfully designed. Upon application of voltage, the absorption and fluorescence spectra of the two polymers can undergo reversible changes, accompanying with the variation of appearance color and emission. By utilizing the controllable characteristics of polymers, the dual-mode display devices are fabricated via a simple spraying method. More interestingly, the color code device was elaborately constructed by adding color change multiplexing to two-dimensional space, thereby achieving high capacity information storage. Moreover, the color code device can also be applied in the multilevel anti-counterfeiting areas. The encrypted information can be dynamically converted under different voltages. The AIE polymers show great promise in the applications of multidimensional information storage and dynamic anti-counterfeiting and the design strategy may provide a new path for advanced information storage and high security technology.

INTRODUCTION

With the development of the big data era, global information is increasing explosively, raising huge challenge to the information storage capacity.¹ Meanwhile, counterfeiting threats to the information security of both individuals and society.²⁻³ Therefore, it is highly desired to realize both high capacity storage of information and multilevel anti-counterfeiting in the same media. To increase the storage capacity of information within the spatially limited volume, information multiplexing shows distinct advantages by expanding the two-dimensional (2D) physical space to the multidimensional space.⁴⁻⁶ A few breakthrough works have been proposed and studied by the addition of distinguishable new dimensions in the basis of 2D space, such as wavelength,⁷⁻⁸ intensity,⁹⁻¹⁰ polarization,¹¹ and lifetime.¹²⁻¹³ In terms of anti-counterfeiting, stimuli-responsive materials have been widely explored to address the counterfeiting challenge because of their unique response properties. The smart materials exhibited obvious change under the stimulus, such as light, electricity, mechanical force, heating, pH, and their combinations.¹⁴⁻²² Especially, some remarkable works achieved multiple transformations of output in response to the stimulus input, rather than just output in a static form, which could further realize multilevel

security.²³⁻²⁶ Consequently, in order to simultaneously achieve the requirements of high capacity information storage and anti-counterfeiting, a suitable medium needs to meet at least two criteria: (1) the expansion of 2D physical space to the multidimensional space, and (2) the multilevel transformations under stimulation. Apparently, it is a great challenge to explore the appropriate system possessing the advantages of both high capacity storage and multilevel security.

Among these stimuli-responsive materials, electrical response materials exhibit desirable features that can be handily combined with the electronic devices for a wide range of applications.²⁷⁻²⁹ Electrochromic and electrofluorochromic materials, typical electrical stimulus materials, have attracted tremendous attention due to the reversible change of optical properties (color, transmission, and fluorescence) by redox-driven electric potentials.³⁰⁻³³ Notably, to address the low fluorescence contrast in solid state, a few electrochromic and electrofluorochromic dual-functional materials have been reported by introducing aggregation-induced emission (AIE) units.³⁴⁻³⁶ Taking advantage of the controllable stimulus change, these materials have been exploited for multicolor displays, smart windows, E-paper, and sunglasses applications.³⁷⁻⁴² However,

less attention has been paid on the anti-counterfeiting application,⁴³⁻⁴⁷ and the actual demand for high capacity storage and multilevel anti-counterfeiting cannot be realized by the reported technology. In principle, considering the characteristics of controllable multiple color and fluorescence of the electrochromic and electrofluorochromic dual-functional materials, it may be possible to simultaneously realize information multiplexing storage and dynamic anti-counterfeiting through elaborate design.

Herein, we put forward a simple but effective strategy for constructing information storage and multilevel anti-counterfeiting device using electrochromic and electrofluorochromic dual-functional AIE polymers. As shown in Figure 1, 4-methoxytriphenylamine (TPA-OMe) was chosen as the electroactive modulator since it is regarded as the shining star in the electrochromic realm owing to its high electrochemical stability and low oxidation potential. To improve the fluorescence intensity of the material in the solid state, two different aggregation-induced emission units of tetraphenylethylene (TPE) and dithiophenyldiphenylethylene (DTDPE) were introduced into the polymer. By changing the structure of polymer backbone, the absorption, fluorescence, and electrical stimulation performance of the two polymers can be well controlled on demand. Under the stimulation of different voltages, the appearance color and fluorescence emission of the two polymers changed obviously. Thanks to their good solubility, the polymers can be used to construct different patterns display and transformation device by spraying method. More excitingly, a three-dimensional color code device was fabricated, and dynamic transformation could be realized under the electrical stimulus, showing potential in multi-dimensional information storage and multilevel anti-counterfeiting applications. To the best of our knowledge, this is the first example of color code device technology based on the electrical stimulus response materials, which may broaden applications of these materials in advanced storage and security areas.

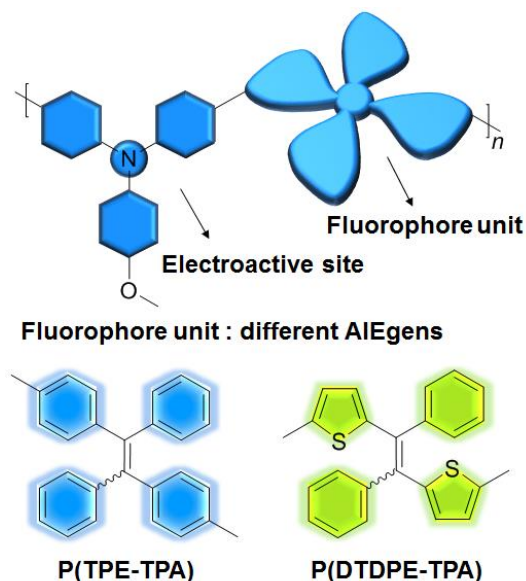


Figure 1. Design principle of the electrical stimulus polymers using different AIE units.

RESULTS AND DISCUSSION

Synthesis and Characterization. The synthetic routes to these two polymers are outlined in Scheme S1, and the synthesis details are shown in Supporting Information. The monomer of TPA-OMe was synthesized according to the reported literature.⁴⁸ and its comonomers of TPE-Br and DTDPE-Br, were synthesized through McMurry coupling. The two polymers were then readily obtained through Suzuki polycoupling. All the monomers and polymers were fully characterized by ¹H and ¹³C NMR spectroscopy and satisfactory results were obtained (Figures S1-S11). These two polymers are soluble in common organic solvents, such as tetrahydrofuran (THF) and chloroform, which facilitates the fabrication of thin films. The decomposition temperatures (T_d , 5% weight loss) of P(TPE-TPA) and P(DTDPE-TPA) were measured as high as 451 and 460 °C by thermogravimetric analysis, and their glass transition temperatures were tested to be 223 and 230 °C by differential scanning calorimetry, respectively (Figure S12). After confirming their excellent thermal properties, the electrochemical properties of the two polymers were measured by cyclic voltammetry. As shown in Figure S13, the polymer films show relatively low onset oxidation voltages (E_{onset}), which were observed at 0.62 V for P(TPE-TPA) and 0.43 V for P(DTDPE-TPA). It is worth noting that E_{onset} of P(DTDPE-TPA) is lower than that of P(TPE-TPA) due to the stronger electron donating ability of thiophene groups than phenyl groups in the polymer main chain.

Photophysical Properties. The UV-vis absorption and photoluminescence (PL) spectra were performed to analyze the photophysical properties of the two polymers, and the data details are summarized in Table S1. As shown in Figure S14, P(TPE-TPA) shows an absorption peak at 372 nm in THF solution. After incorporation of the electron donating thiophene groups, the absorption peak of P(DTDPE-TPA) is red-shifted to 441 nm in THF solution. P(TPE-TPA) exhibits green emission with PL peak at 513 nm in dilute THF solution, accompanying with a absolute fluorescence quantum yield (Φ_F) as low as 2.2%. Because of more planar conformation and strong π -conjugation, P(DTDPE-TPA) shows orange emission with red-shifted PL peak at 585 nm with a Φ_F value of 0.7%. In contrast to the faint emission in THF solution, the bright emission of the two polymers in the film states could be observed. The Φ_F values of P(TPE-TPA) and P(DTDPE-TPA) were dramatically improved to 52.9 and 15.6% in film states, respectively, indicative of the typical AIE characteristic.

To further investigate the AIE activity, the emission behaviors of the two polymers were analyzed in THF/water mixtures with different water fractions (f_w). As displayed in Figure 2, the Φ_F values of the two polymers increase significantly with an increase in f_w , confirming the AIE activity. The Φ_F values of P(TPE-TPA) and P(DTDPE-TPA) in THF/water mixtures with f_w of 90% are 21- and 15-fold higher than that in THF solutions, respectively. The AIE features of P(TPE-TPA) and P(DTDPE-TPA) also can be vividly seen from their solution photos in THF and THF/water mixtures with f_w of 90% taken under UV irradiation at 365 nm. The THF solution exhibits faint emission while the THF/water mixture emits strong fluorescence. The PL spectra of P(TPE-TPA) and P(DTDPE-TPA) in

THF/water mixtures with different f_w further confirm their AIE behaviors (Figure S15). The obvious AIE phenomenon can be explained as follows. In the solution state, the active intramolecular motions turn on the non-radiative decay of the excited state, resulting in weak emission. With the formation of aggregates, the intramolecular rotations are restricted, and the nonradiative decay channels are obstructed in the aggregate state, prompting the enhancement of fluorescence intensity.

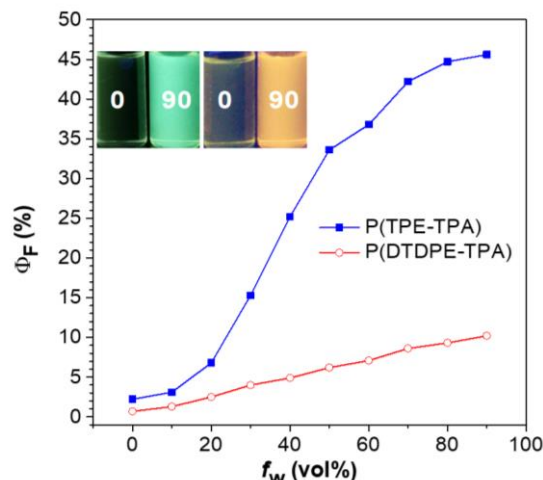


Figure 2. Plots of absolute PL quantum yield (Φ_F) values versus f_w in THF/water mixtures. Inset: the photographs of the polymers in THF and THF/water mixtures with a f_w of 90%.

Electrochromic and Electrofluorochromic Performance. The electrochromic properties of the two polymers in film state were studied on the electrochemical workstation combined with UV-vis spectroscopy. As shown in Figure 3A, with the applied potential increasing from 0.0 to 1.2 V, the absorption band shorter than 440 nm gradually decreases while new absorption band in longer wavelength (500–800 nm) emerged and increases progressively, which could be attributed to the formation of cation radicals in the polymer main chains. The color of the P(TPE-TPA) film changed from green (0.0 V) to brown (1.0 V) and finally to black (1.2 V). The similar modulated behaviors of P(DTDPE-TPA) film were observed after increasing the potential from 0.0 to 1.0 V (Figure 3B). The neutral absorption peak centered at 435 nm gradually decreases while the new absorption peak at around 633 nm grows up increasingly, accompanying with the color change from orange to black. Then, after applying sequential square wave potential, the response time and switching stability were characterized in the kinetics studies by monitoring the absorption changes. The switching time of the film reaching 90% of its maximum absorption change was calculated. As depicted in Figure S16, the coloring/bleaching response time was evaluated as 2.2/4.0 s for P(TPE-TPA) and 2.1/3.8 s for P(DTDPE-TPA). As displayed in Figure S17, the two polymers maintain good recoverability in 50 cycles. In general, they can separately exhibit obvious color changes in a short time through electrical stimulation, which is conducive to the anti-counterfeiting applications.

Then, we studied the change of fluorescence using different positive potentials. As shown in Figure 4A, the strong

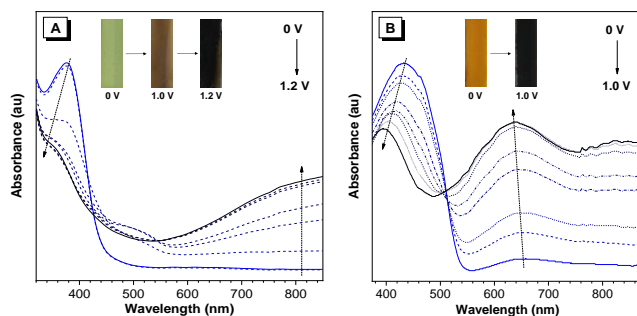


Figure 3. UV spectra of (A) P(TPE-TPA) and (B) P(DTDPE-TPA) thin film electrodes in 0.1 M TBAP/ CH_3CN solution under different voltages.

green fluorescence of P(TPE-TPA) film was quenched to dark green as applied potential around 0.7 V, then almost vanished at 1.0 V. Similarly, the PL intensity of P(DTDPE-TPA) film decreases with increasing potentials from 0 to 0.7 V, accompanying with orange fluorescence to non-emissive one (Figure 4B). The quenching of fluorescence is attributed to the generating cationic radicals, which act as an effective fluorescence quencher that causes the large overlap between the absorption and the emission spectra in the oxidation process.⁴⁹ Due to the introduction of the AIE units to the polymers, the high fluorescence on/off contrast ratios were calculated to be 282 for P(TPE-TPA) and 146 for P(DTDPE-TPA), which are higher than that those in most reported works.^{34,36,50} The fluorescence off/on response time was estimated at 90% of the full switching of the film state (Figure S18), and switching time is 1.4/38 s for P(TPE-TPA) and 0.8/36 s for P(DTDPE-TPA). The shorter response time of P(DTDPE-TPA) may be owing to the introduction of thiophene units in the polymer backbone which make the polymer more conjugated than P(TPE-TPA), thereby enhancing the intramolecular charge transporting ability.⁴⁹ After switching for 50 cycles, the two polymers maintain moderate reversibility (Figure S19). It is worth noting that the voltages required for complete fluorescence quenching of the two polymers are different, which is beneficial to the later electric stimulus applications.

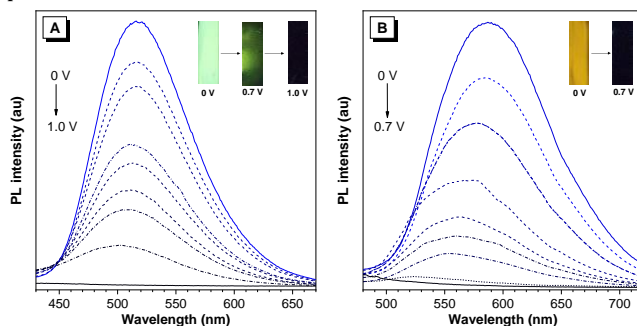


Figure 4. PL spectra of (A) P(TPE-TPA) and (B) P(DTDPE-TPA) thin film electrodes in 0.1 M TBAP/ CH_3CN solution under different voltages.

Dual-Mode Display Device. Encouraged by the polymer performance under electrical stimulation, we first constructed a simple display device with the configuration of glass/ITO/polymer/ITO/glass. As illustrated in Figure 5A, the mold was first designed according to the content and shape of the display pattern. Then, it was fixed on the ITO

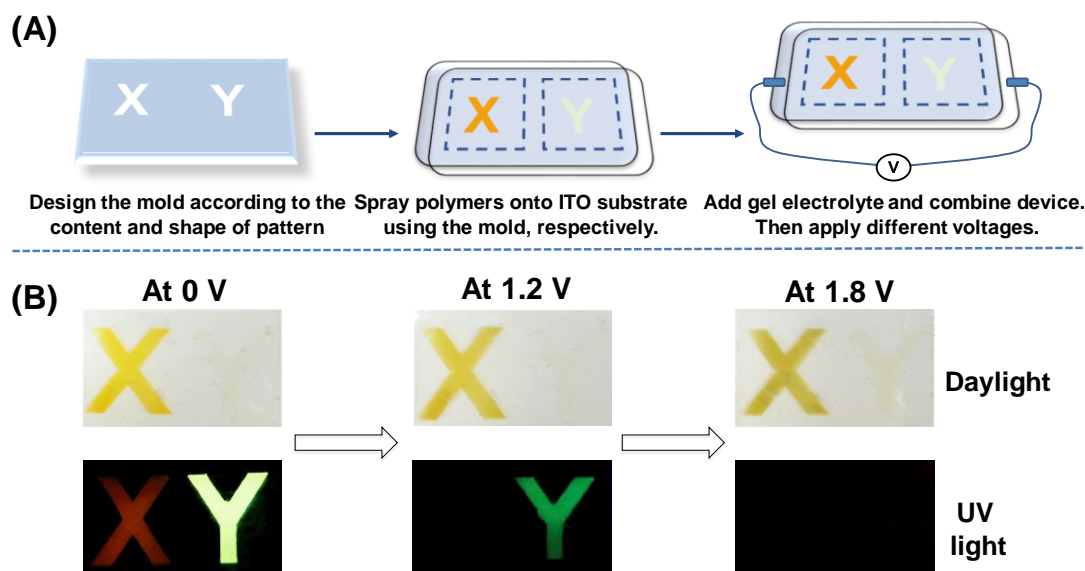


Figure 5. (A) Scheme illustration of the preparation procedures of the device. (B) Photographs showing the changes of English letters device with different voltages under daylight and UV light. The size of the ITO substrate is 4.5×5.5 cm.

substrate, and the polymer materials were sprayed onto the designated area. To prevent the leakage problem, gel electrolyte (CAN/TBAP/PC/PMMA = 70:3:20:7) was selected to combine the device. Initially, the device with English letters pattern was fabricated (Figure 5B and Movie S1 in the Supporting Information). Under daylight, the appearance color of “X” and “Y” patterns changed significantly with the increasing voltages. While under the UV light, the orange emission of “X” and green emission of “Y” can be seen at 0 V. Since the two polymers responded differently to voltages, the “X” first rapidly experienced fluorescence quenching when the positive voltage was increased to 1.2 V. At this moment, only the “Y” can display. Applying voltage to 1.8 V, both the “X” and “Y” patterns disappeared completely. Therefore, the device can be applied in dual-mode display under daylight and UV light. To prove the universality of this approach, we also constructed a numerical display device (Figure S20 and Movie S2 in the Supporting Information). In order to increase the diversity of color, a blue fluorescence polymer P(TPE-NB) was introduced into the device (Figure S21), and its color cannot be changed under electrical stimulation. The numerical device can display three different numbers “8”, “3”, and “1” at 0, 1.2, and 1.8 V, respectively. These results demonstrate that the device design strategy through a simple spraying method can realize the dual-mode display and dynamic conversion of the patterns.

High Capacity Storage Device. Inspired by above different colors display devices, we speculated that the realization of high capacity information storage is possible by constructing multidimensional devices. As delineated in Figure 6, the designed color code device increases the color change multiplexing in the basis of the 2D physical space and expands into multidimensional space, thereby increasing the information density per unit area. By scanning the color code, the information could be easily read out by smartphone and programmed by the user in advance to load specific webpage. The device could be pre-

pared by the use of above mentioned method (glass/ITO/polymer/ITO/glass). Three different polymers (P(TPE-TPA), P(DDPE-TPA), and P(TPE-NB)) were selectively sprayed onto designated grids on the ITO substrate according to the specified combination. The arrangement of the three polymers in the grids and the obtained total information can be calculated by mathematical combination, as shown in the inset table (Figure 6). When only one polymer was sprayed onto ITO, there are three combinations in the grids that can give two different kinds of information under daylight and UV light. In the case of two polymers, there are two options in each grid. At the same time, the color of the device will change once under electrical stimulation, accordingly four different messages of one device will be stored under daylight and UV light. In the presence of three polymers, there are three choices in each grid. And the information changes twice under electrical stimulation, so six different kinds of information of one device can be obtained. For example, the total stored information over five trillions can be achieved by the use of 5×5 grids, which allows to overcome the capacity limit dictated by 2D space. If the number of grids is further increased, the obtained information number could be almost endless, displaying the ultra-high capacity storage. The realization of high capacity storage device is attributed to the increase of color dimensional based on 2D physical space, and then the color transformation under electrical stimulus further increases the information storage capacity.

Multilevel Anti-Counterfeiting Device. Because of these dynamically controllable electrochromic and electrofluorochromic features, the color code device also offers a promising approach in information anti-counterfeiting application. One color code device made of three polymers based on one specific combination is shown in Figure 7. Under different potentials, the color and fluorescence intensity of certain areas in the color code device would be changed to some extent, and accordingly a dynamic

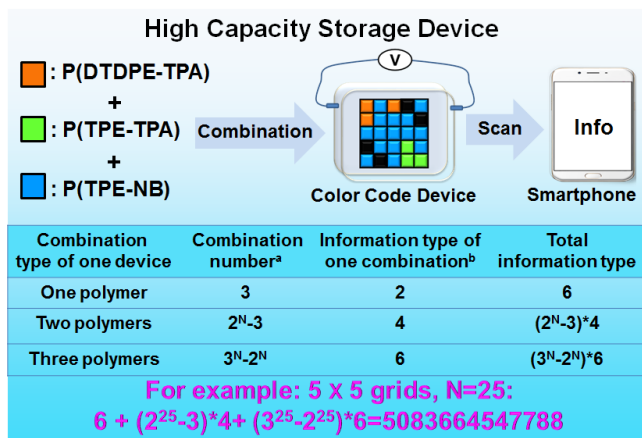


Figure 6. Scheme illustration of the high capacity storage device. ^aThe combination number is based on the mathematical arrangement. ^bTotal information types include that were observed under daylight, UV light, and the transformation of information content by electrical stimuli. For 5 × 5 grids, N=25: color code devices can store over five trillions of information type.

manipulation was achieved. The information reading through smartphone under daylight was defined as wrong, whereas only the information reading under UV light was defined as correct. Hence, different true information can only be read out by smartphone upon UV irradiation. The security of information encrypted through this new method is extremely high. Counterfeiter must identify all (not a part of them) the following security measures: (1) the right combination of the three polymers; (2) the right stimulus (electricity); (3) the correct observe condition (UV light); (4) the proper voltage value. Consequently, only the authorized individual who knows the correct decoding rules can access the confidential information, greatly improving the security level of the information.

Based on the above design strategy, the color code device was easily fabricated. Initially, the device based on one combination was successfully constructed by using two polymers (Figure S22 and Movie S3 in the Supporting Information). On the basis, we also fabricated the other color code device based on a new combination using three polymers (Figure 8 and Movie S4 in the Supporting Information). The correct encoded information in this device can only be read out under UV light, while the information can be recognized as wrong information under daylight by smartphone scanning. In the initial state, the blue, orange, and green fluorescence of the color code were clearly seen, and the specific information (Info A) can be read out from the smartphone when the device was irradiated by UV light. Then, the color code can be transformed by the voltage stimulation. After increasing the voltage to 1.2 V, the orange fluorescence of P(DTDPE-TPA) was quenched, only the blue and green fluorescence emission color code could be identified by smartphone, thus obtaining another information (Info B). The voltage was further increased to 1.8 V, the P(TPE-TPA) regions became nonluminous, and the color code device only emit blue light. Info C could be accessed by scanning smartphone. Under the modulated voltages, the Info A, Info B, and Info C can achieve dynamic transformation. These device results indicate that different true information were decrypted upon UV irradiation

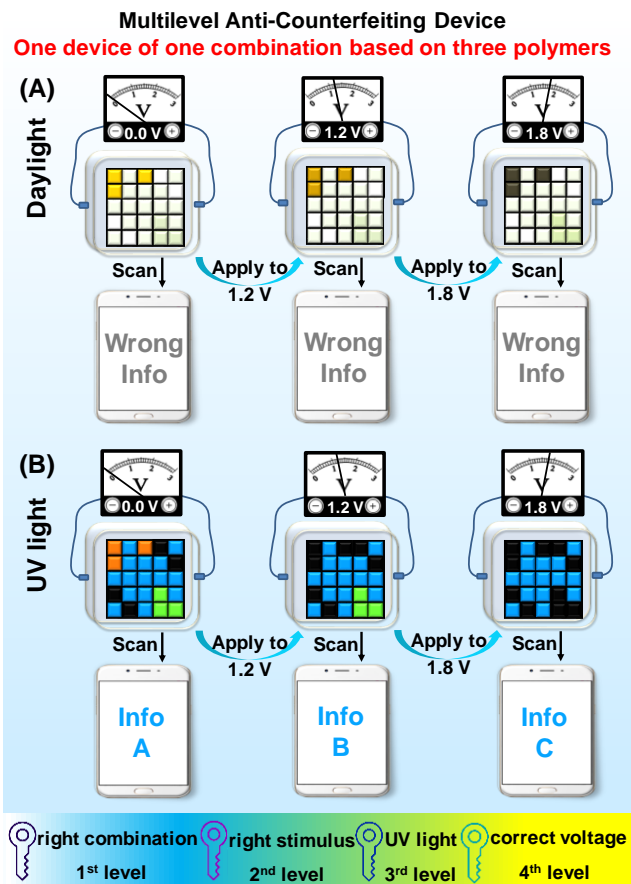


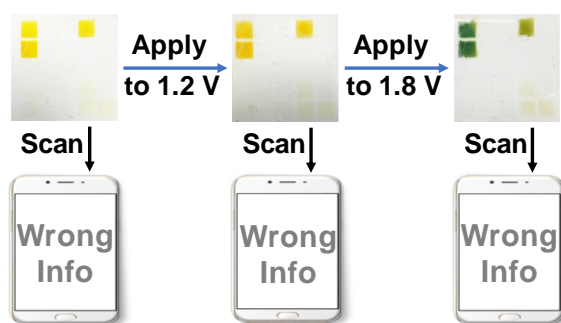
Figure 7. The schematic illustration showing multilevel anti-counterfeiting device based on one combination of three polymers under (A) daylight and (B) UV light.

with various voltages stimulation. Hence, only the authorized individual knowing the correct encryption algorithm has opportunity to obtain the specific information, which greatly promotes the security to a higher level.

CONCLUSIONS

We rationally designed and facilely prepared two electrochromic and electrofluorochromic dual-functional AIE polymers of P(TPT-TPA) and P(DTDPE-TPA), based on which high capacity storage and multilevel anti-counterfeiting were simultaneously realized. By using a simple spraying method, the dual-mode display devices with different patterns (English letters and numeric) were successfully constructed. The high capacity information storage was achieved with the color change multiplexing, which overcomes the limitation of the 2D space. Taking advantage of the controllable color change feature, the color code device can also be applied in the multilevel anti-counterfeiting areas, which realizes the dynamic transformations of Info A, Info B, and Info C. Thus, this work provides a new insight into the exploration of the electrochromic and electrofluorochromic dual-functional AIE polymers in information storage and dynamic security applications, which may open up new avenues for electrical stimulus response materials.

(A) Under Daylight



(B) Under UV light

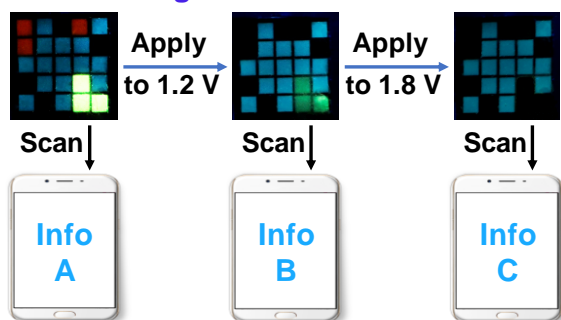


Figure 8. The color code device based on three polymers with different voltages under (A) daylight and (B) UV light. The size of the ITO substrate is 4.8×4.8 cm.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website. Experimental procedures and the supporting figures referenced in the manuscript. Movies of the English letters device, numerical device, and color code devices.

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Notes

The authors declare no competing financial interests.

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