Novel Aromatic Polyamides Containing 2-Diphenylamino-(9,9-dimethylamine) Units as Multicolored Electrochromic and High-Contrast Electrofluorescent Materials

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ABSTRACT: A series of electrochromic and photoluminescence-active polyamides 4a-4e were prepared from a novel dicarboxylic acid, N,N-di(4-carboxyphenyl)-2-amino-9,9-dimethylfluorene, and five diamines via a condensation polymerization. These polyamides were amorphous and readily soluble in many solvents. The glass transition temperatures were in the range of 281–339 °C and the 10% weight loss temperatures in nitrogen were in excess of 490 °C. The polyamides exhibited strong fluorescence in either solution or solid states. The polyamides 4a-4d showed reversible electrochemical redox with color changing from colorless to grey-green. Specially, the polyamide 4e with 2-diphenylamino-(9,9-dimethylamine) group in both diamine and dicarboxylic acid residues exhibited multicolored electrochromic behaviors. Furthermore, the fluorescence of these polyamides could be reversibly electroswitched with a high contrast up to 221.4, enabling their potential applications in dual-switching electrochromic/electrofluorescent materials.

KEYWORDS: electrochemistry; electrochromism; electrofluorescence; fluorene; polyamides; triphenylamine

INTRODUCTION Electrochromism is defined as the reversible color change of materials by application of an electric field. Since the first electrochromic material WO3 was reported by Deb in 1969,1 various electrochromic materials have been developed including inorganic metal oxides;2,3 transition metal complexes4 and organic materials.5–7 Several such materials have already been commercialized in the fields of smart windows, mirrors, and displays.8–10 Recently, electronically dimmable windows were developed by Gentex to apply in the new Boeing 787 Dreamliner. Similarly, electrofluorescence refers to the fluorescence change of materials controlled by electrochemical oxidation or reduction. This unique stimuli-responsive fluorescence characteristic has attracted more and more attention for their potential applications in bioanalysis11,12 and fluorescence imaging.13,14 Specifically, dual-mode switching of both coloration and emission in displays could be achieved by combining electrochromic and electrofluorescent technologies, thus the novel displays will be highly visible in either bright or dark environments. To date, several dual electrochromic/electrofluorescent materials have been reported.15–17 However, most of the existing materials lack enough stability and high-contrast of switching. Thus, there is still a great requirement to develop versatile bifunctional materials to fit into the application of dual-mode displays in the future.

Triphenylamine with propeller starburst structure is well-known for the strong electron donating and excellent hole-transmission capability.18 Triphenylamine derivatives have been thoroughly researched and applied in organic light emitting diodes (OLEDs),19,20 dye-sensitized solar cells (DSCs)21,22 and memory devices.23,24 In particular, triphenylamine derivatives could switch their colors reversibly and stably during the oxidation-reduction process as long as the para-position of triphenylamine is protected effectively.25 Thus, triphenylamine-containing materials are promising as an attractive family of electrochromic materials.26–30 Since 2005, a lot of high performance polymers with
triphenylamine unit as the redox-chromophore for applying in electrochromic materials have been designed and synthesized.31–35 The introduction of packing-disruptive triphenylamine units in polymer backbone will greatly improve the solubility of the resulting polymers, which is beneficial for fabricating large-area electrochromic device by convenient spin coating. However, fluorene derivatives possessing relatively large band gaps are considered as one of the most suitable blue emission materials.36 They have excellent quantum efficiencies, electron mobilities and thermal stabilities. Moreover, fluorene-triphenylamine derivatives received extra attention as they could be used as hole-transmission emitters in the OLEDs.37 Inspired by the attractive properties associated with the triphenylamine and fluorene units, we are expected to exhibit enhanced fluorescent properties, because the para-position of triphenylamine is well protected. However, the polyamides derived from aromatic dicarboxylic acids exhibited poor fluorescence. Furthermore, the polyamide derived from the corresponding polyamides based on the dinitrile compound 1 in 51.1% with a melting point of 203 °C. IR (KBr): 2220 cm⁻¹ (C=O stretch). 1H NMR (300 MHz, DMSO-d₆, ppm): 7.88 (d, J = 8.1 Hz, 1H), 7.78 (d, J = 7.0 Hz, 1H), 7.73 (d, J = 8.8 Hz, 4H), 7.53 (d, J = 5.2 Hz, 1H), 7.44 (d, J = 1.9 Hz, 1H), 7.3 – 7.27 (m, 2H), 7.20 – 7.10 (m, 5H), 1.39 (s, 6H).

Synthesis of N,N-di(4-carboxyphenyl)-2-amino-9,9-dimethylfluorene

A mixture of 10.9 g (195 mmol) of Potassium hydroxide and 8 g (19.5 mmol) of the dinitrile compound 1 was dispersed in 160 mL of ethanol/water (7/9) solution, and stirred at 90 °C for about 5 days until no further ammonia released. The reaction solution was cooled and the pH value was adjusted by hydrochloric acid to 3 around. The resulting yellow precipitate was collected by filtration and then washed with water thoroughly. The crude product was purified by recrystallized from acetic acid/water. Then the dicarboxylic acid 2 was collected and dried under vacuum (66.1% of yield, mp = 320 °C). IR (KBr): 3400–2700 cm⁻¹, 1674 cm⁻¹ (−COOH stretch). 1H NMR (300 MHz, DMSO-d₆, ppm): 12.69 (s, 2H, −COOH), 7.85–7.82 (m, 5H, H₁, H₂, H₃, H₄), 7.78 (d, J = 6.6 Hz, 1H, H₅), 7.32 (d, J = 8.7Hz, 1H, H₆), 7.39–7.25 (m, 3H, H₇, H₈, H₉), 7.06–7.14 (m, 5H, H₁₀, H₁₁), 1.38 (s, 6H, −CH₃). 13C NMR (75 MHz, DMSO-d₆, ppm): 166.77, 155.36, 153.46, 150.48, 144.95, 137.84, 136.09, 130.95, 127.21, 127.10, 125.56, 124.63, 122.69, 122.05, 121.53, 120.98, 119.96, 46.60, 26.61, (−CH₃).

Synthesis of Polyamides

Five polyamides were prepared via a condensation polymerization from N,N-di(4-carboxyphenyl)-2-amino-9,9-dimethylfluorene and five diamines (as shown in Scheme 2). The resultant polyamides were abbreviated to 4a–4e, respectively. A typical polymerization process of 4b was given as follow. A mixture of 0.4492 g (1 mmol) of N,N-di(4-
carboxyphenyl)-2-amino-9,9-dimethylfluorene, 0.2002 g (1 mmol) of 4,4'-oxydianiline, 0.12 g of calcium chloride, 0.5 mL of pyridine, 1 mL of TPP and 2.5 mL of NMP were heated with stirring at 120 °C for 3 h. After cooling, the resulting viscous polymer solution was poured slowly into 200 mL of methanol with stirring, producing a fiber-like precipitate. The precipitate was washed thoroughly with hot water and methanol, and then dried under vacuum at 100 °C. Reprecipitations of the polymer by DMAC/ethanol were carried out twice for further purification. 1H NMR (300 MHz, DMSO-d_6, δ, ppm): 10.18 (s, 2H, amide N-H), 7.95 (d, J = 8.5 Hz, 4H, H_d), 7.86 (d, J = 8.2 Hz, 1H, H_i), 7.83–7.72 (m, 5H, H_e–H_j), 7.54 (d, J = 7.0 Hz, 1H, H_h), 7.42–7.26 (m, 3H, H_e + H_g + H_h), 7.17 (d, J = 8.5 Hz, 4H, H_b), 7.11 (d, J = 8.5 Hz, 1H, H_i), 7.01 (d, J = 8.7 Hz, 4H, H_b), 1.41 (s, 6H, —CH_3).

The polymer films were prepared as follows. A solution of the polymer was obtained by dissolving about 0.3 g of sample in 6 mL of DMAc. The resulting solution was then poured into a 6 cm glass Petri dish, which was placed in the oven at 90 °C for 10 h to release the solvent slowly. After that, the damp-dry film was further dried at 160 °C for 10 h under vacuum. These as-prepared films were about 35–45 μm in thickness and subsequently used for solubility tests, X-ray diffraction measurements and thermal analyses.

Measurements
Fourier transform infrared (FTIR) spectra were recorded through a Bruker Vector 22 spectrometer at a resolution of 4 cm⁻¹ in the range of 400-4000 cm⁻¹. Nuclear magnetic resonance (NMR) spectra were determined on a BRUKER-300 spectrometer at 300 MHz for ¹H NMR and 75 MHz for ¹³C NMR in deuterated DMSO. Inherent viscosities (η_inh) were measured through an Ubbelohde viscometer with a 0.5 g/dL of DMAc solution at 25°C. Differential scanning calorimetric (DSC) analysis was performed on a TA instrument DSC Q100 at a scanning rate of 10°C/min in a nitrogen flow of 50 mL/min. Thermo gravimetric analysis (TGA) was conducted with the TA 2050, with a heating rate of 10°C/min under nitrogen and air atmosphere. Wide-angle X-ray diffraction (WXRD) measurements were carried out on a Rigaku/max-ra diffractometer equipped with a Cu Kα radiation source. Electrochemistry measurements were performed on a CHI 660e electrochemical analyzer. Cyclic voltammetry (CV) was conducted with the use of a three-electrode cell. The working electrode was prepared by drop-coating of the polymer solutions onto ITO glass substrate (The area of polymer films was about 0.5 × 2 cm²). A platinum wire was used as an auxiliary electrode and a homemade Ag/AgCl, KCl (sat.) was used as a reference electrode. Ultraviolet-visible (UV-vis) spectra were measured using a PerkinElmer Lambda 950 spectrophotometer. PL spectra and fluorescent quantum yield were determine with an Edinburgh FLS920.
fluorescence spectrophotometer. Fluorescent quantum yield ($\Phi_F$) was determined using a calibrated integrating sphere.

**RESULTS AND DISCUSSION**

**Monomer Synthesis**

As shown in Scheme 1, the new dicarboxylic acid with DPA-MeF group was synthesized via a multistep route. First, the dinitrile compound 1 was successfully synthesized through the CsF-assisted $N,N$-diarylation reaction of 4-fluorobenzonitrile and 2-amino-9,9-dimethylfluorene. Then the alkaline hydrolysis and acidification reaction were employed to synthesize the dicarboxylic acid 2. FTIR and NMR spectroscopic techniques were utilized to identify the structures of the monomers. In the FTIR spectrum, the characteristic bands of cyano group at around 2220 cm$^{-1}$ disappeared after alkaline hydrolysis reaction. Meanwhile, new stretching absorptions corresponding to the carboxylic acid group appeared at 1674 cm$^{-1}$ (C=O stretch) and 2700–3400 cm$^{-1}$ (O–H stretch; Supporting Information Fig. S1), indicating the formation of the new dicarboxylic acid. Figure 1 illustrates the $^1$H NMR and $^{13}$C NMR spectra of the dicarboxylic acid monomer 2 with the assignments for the proton and carbon signals. All the NMR signals support the proposed molecular structure of the target dicarboxylic acid with DPA-MeF group.

**Polymer Synthesis and the Basic Properties**

A novel series of polyamides with DPA-MeF group were synthesized via a condensation polymerization from the dicarboxylic acid monomer 2 and five different diamines 3a-3e (Scheme 2). All the polymerizations proceeded homogeneously and yielded highly viscous polymer solutions. When pouring the resulting viscous solutions into methanol, all these polymers precipitated in a yellow and fiber-like form. These samples were purified further by reprecipitation method using DMAc/ethanol. The inherent viscosities and molecular weights of these polyamides are summarized in Table 1. All these high molecular weights polyamides could be solution-casted into free-standing films. All these polyamides exhibited typical absorptions at 1667 (C=O stretching) and 3310 cm$^{-1}$ (N–H stretching), sustaining the formation of the amide linkage. $^1$H NMR spectra of these polyamides were illustrated in Figure 2 and Supporting Information Fig. S1), indicating the formation of the new dicarboxylic acid. Figure 1 illustrates the $^1$H NMR and $^{13}$C NMR spectra of the dicarboxylic acid monomer 2 with the assignments for the proton and carbon signals. All the NMR signals support the proposed molecular structure of the target dicarboxylic acid with DPA-MeF group.

**TABLE 1 Inherent Viscosities, Molecular Weights, and Solubilities of the Polyamides**

| Sample | $\eta_{inh}$ (dL/g)$^a$ | $M_n$ | $M_w$ | PDI | DP | Solvents$^c$ |
|--------|-----------------|------|------|-----|----|-----------|
| 4a     | 0.71            | 77,000 | 57,400 | 1.34 | 107 | ++ ++ ++ + -- |
| 4b     | 0.77            | 76,300 | 55,100 | 1.38 | 87  | ++ ++ ++ + -- |
| 4c     | 0.60            | 88,300 | 59,400 | 1.49 | 78  | ++ ++ ++ ++ ++ +-- |
| 4d     | 0.64            | 78,400 | 51,500 | 1.52 | 67  | ++ ++ ++ ++ ++ +-- |
| 4e     | 0.72            | 63,100 | 45,800 | 1.38 | 58  | ++ ++ ++ ++ ++ +-- |

$^a$ Inherent viscosities were measured at a concentration of 0.5 g/dL in DMAc at 25°C.

$^b$ Relative to polystyrene standard, using DMF as the eluent.

$^c$ Qualitative solubilities were tested with 10 mg of polymers in 1 mL of solvent.

++: soluble at room temperature; +: soluble on heating; +−: partially soluble; −: insoluble even on heating.

**TABLE 2 Thermal Properties of the Polyamides**

| Polymer | $T_g$ $^a$ | $T_{d10}$ $^b$ | N$_2$ | Air | Char yield (wt %)$^c$ |
|---------|------------|-----------------|------|-----|-----------------------|
| 4a      | 299        | 498             | 492  | 65  |
| 4b      | 281        | 495             | 487  | 59  |
| 4c      | 302        | 493             | 491  | 60  |
| 4d      | 339        | 498             | 497  | 62  |
| 4e      | 284        | 510             | 503  | 64  |

$^a$ Obtained at the baseline shift in the second heating DSC traces, with a heating rate of 10°C/min under N$_2$.

$^b$ Decomposition temperature at which a 10% weight loss was recorded via TGA at a heating rate of 10°C/min.

$^c$ Residual weight percentage at 800°C in N$_2$.
Information Figure S2, all of which displayed the resonance signals at around 10.1 ppm, indicating the formation of amide linkages. The spectra agreed well with the desired structure of the polyamides.

The solubilities of the polyamides were examined by dissolving 10 mg of samples in 1 mL organic solvents with the results listed in Table 1. All of the polyamides could dissolve in polar solvents such as NMP, DMAc, DMF, and DMSO. In particular, the polyamide 4c exhibited better solubility in less polar solvent (THF and CHCl₃) due to its improved free-volume induced by the hexafluoroisopropylidene group in the polymer backbone. The excellent solubility is much favorable for the fabrication of large-area thin film devices in practical application through convenient spin-coating or inkjet-printing processes. Moreover, the WXRD patterns of these film samples (Supporting Information Fig. S4) showed similar broad peaks in the range of 18–32°, which were characteristic diffractions of amorphous polymers. When applied in flexible optoelectronic devices, the amorphous structure is a basic requirement. The excellent solubilities and amorphous properties of these polyamides mainly result from a fact that the bulky DPA-MeF group greatly reduced the close packing of the polymer chains and their interchain interactions.

Thermal Properties
The thermal properties of these polyamides were evaluated by means of TGA and DSC, with the data summarized in Table 2. Generally, the Tₘ value depends on the molecular packing and the stiffness of polymer structure. The Tₘ values of these polymers ranged from 281 to 339 °C, and the lowest Tₘ value of the polyamide 4b was predicted because of its flexible ether linkage in the backbone. No clear melting endotherms were observed on the DSC curves, which further supports the amorphous nature of these polyamides. The TGA curves (in both air and nitrogen atmospheres) were showed in Figure 3. During its process of decomposition, the 10% weight loss temperatures in nitrogen and air were recorded in the range of 493–510 °C and 487–503 °C, respectively. The carbonized residue of these aromatic polymers accounted for up to 59% at 800 °C in nitrogen atmosphere ascribed to their high aromatic content. The excellent thermal properties are profitable for largely extending their service life in optoelectronic devices.

Optical Properties
Optical behaviors of the polyamides were investigated by UV–vis and PL spectroscopy with the results summarized in Table 3. As shown in Figure 4, the polyamides exhibited maximum absorption peaks at around 355–366 nm for NMP solution and 350–364 nm for solid films, which are attributed to π–π* transition of DPA-MeF moiety. The absorption edges of the polyamide films extended to 413–429 nm, from which the optical band gaps were estimated to be 2.89–3.00 eV. The polyamide solutions exhibited strong PL emission at around 448–492 nm with quantum yields ranging from 2.0 to 31.4%. The lowest quantum yield of 4e could be attributed to an increased nonradiative decay resulted from its greater conformational mobility. Compared with the

![Figure 3](https://example.com/image3.png)

**TABLE 3** Optical and Electrochemical Properties of the Polyamides

| Polymer | Abs. max (nm) | PL max (nm) | φ_R (%) | Abs. onset (nm) | Abs. max (nm) | φ_R (%) | E_{onset} (eV) | E_{1/2} (eV) | E_{1/2} (eV) | E_g (eV) | HOMO (eV) | LUMO (eV) |
|---------|---------------|-------------|--------|----------------|---------------|--------|---------------|-------------|-------------|---------|-----------|-----------|
| 4a      | 365           | 448         | 9.2    | 417            | 350           | 7.8    | 0.99          | 1.05        | –           | 2.97    | 5.40      | 2.43      |
| 4b      | 355           | 452         | 25.7   | 416            | 359           | 19.1   | 0.98          | 1.05        | –           | 2.98    | 5.40      | 2.42      |
| 4c      | 357           | 463         | 32.9   | 413            | 359           | 23.4   | 0.95          | 1.05        | –           | 3.00    | 5.40      | 2.40      |
| 4d      | 355           | 454         | 34.1   | 415            | 364           | 25.6   | 0.96          | 1.03        | –           | 2.99    | 5.38      | 2.39      |
| 4e      | 366           | 492         | 2.0    | 429            | 353           | 1.9    | 0.66          | 0.81        | 1.19        | 2.89    | 5.16      | 2.27      |

* The polymer concentration was 10⁻⁵ mol/L in NMP.
* They were excited at the Abs_max for the solution states.
* The quantum yield was tested by using a calibrated integrating sphere.
* E_{1/2} (Average potential of the redox couple peaks).

* The data were calculated by the equation: E_g = 1240/λ_{onset} (energy gap between HOMO and LUMO).
* The HOMO energy levels were calculated from CV and were referenced to ferrocene (4.8 eV).
* LUMO = HOMO – E_g.
corresponding polyamides based on diamine containing DPA-MeF group, these polyamides exhibited enhanced fluorescence properties because of their more extended conjugation benzoyl structures. To get more insight into this phenomenon, TD-DFT calculations were applied to clarify the nature of electron transitions of the two model compounds with different amide structures. As depicted in Figure 5, in the case of the model compound derived from DPA-MeF-based diamine, the HOMO level was located at DPA-MeF moiety, while the LUMO level was located at benzoyl moiety. As a consequence, the CT leads to a nonradiative transfer of energy, which would result in the low quantum yield. However, for the model compound derived from DPA-MeF-based dicarboxylic acid, the excited transition from HOMO to LUMO delocalized over the DPA-based benzoyl moiety, implying the locally excited transition. Therefore, the model compound derived from DPA-MeF-based dicarboxylic acid revealed higher PL emission than the model compound derived from DPA-MeF-based diamine, and the PL properties of the polyamides could be enhanced by altering the amide orientation. In particular, it is worth noting that these polyamides also exhibited strong fluorescence in the solid states. However, the fluorescence quantum yields of polymer films still decreased compared with that of polyamide NMP solutions, which may be ascribed to the competition between the aggregation-caused quenching and the aggregation-induced emission.

![FIGURE 4](https://example.com/figure4.png)

**FIGURE 4** UV–vis absorption spectra of polyamides 4a–4e in NMP solutions (a) and solid films (b). PL spectra of polyamides 4a–4e (c). The fluorescence photographs of their NMP solutions and solid films (d). [Color figure can be viewed at wileyonlinelibrary.com]

![FIGURE 5](https://example.com/figure5.png)

**FIGURE 5** Calculated molecular orbitals of the model compounds (TD-DFT method at the B3LYP/6-31G (d, p)). The insets show the fluorescence photographs of their NMP solutions. [Color figure can be viewed at wileyonlinelibrary.com]
Electrochemical and Electrochromic Properties

The electrochemical properties were investigated by CV with a three-electrode system. The polyamide films coated on ITO substrates were used as working electrodes. In Figure 6, the polyamides 4a-4d showed a reversible redox couple with oxidation half-wave potential ranging from 1.03 to 1.05 eV, which indicates that the diamine structure has a weak influence on the oxidation of the polyamides with DPA-MeF group. Compared with the corresponding polyamides derived from DPA-MeF-based diamine, the oxidation of these synthesized polyamides here are less facile due to the strong electron-withdrawing effect of carbonyl groups. As expected, the polyamide 4e exhibited two reversible oxidation redox couples because two electrons successively transferred from the nitrogen atoms in the two different kinds of DPA-MeF groups. The first oxidation \( (E_{1/2}) \) was related to the electron loss from the DPA-MeF group of the diamine, while the second oxidation resulted from the DPA-MeF group of the dicarboxylic acid. The highest occupied molecular orbital (HOMO) energy levels of these polyamides were calculated from \( E_{1/2} \) through comparing with the ionization potential of ferrocene (4.8 eV), and the lowest unoccupied molecular orbital (LUMO) levels were estimated from the equation: 

\[
LUMO = HOMO - E_g.
\]

All the details of the electrochemical data as well as HOMO and LUMO levels are summarized in Table 3.

In the CV measurement, the polyamide films were observed to switch their colors obviously with CV scanings.
Therefore, the spectroelectrochemical techniques were performed to evaluate their electrochromic properties. Here, we used the polyamide 4d (similar to the other 4a–4c counterparts) as an example to investigate the absorption changes at different applied potentials (Fig. 7). Upon the electro-oxidation arising from 0 to 1.3 V, the intensity of the characteristic absorption peak of DPA-MeF at 358 nm gradually decreased while two new peaks at 423 and 890 nm grew up attributed to the formation of the stable cation radical. Meanwhile, the color of the polyamide film changed drastically from colorless neutral state to gray-green oxidation state. Due to the unique electrochemical properties, polyamide 4e might possess distinct electrochromic behavior compared with the aforementioned polyamides. As shown in Figure 8, the polyamide 4e film exhibited double color changes, arising from two different DPA-MeF groups. When the applied potential was increased to 0.9 V, the intensity of the absorption peak at 362 nm gradually decreased while two new peaks appeared at 430 and 860 nm. With the potential increased to 1.5 V, the intensity of the absorption bands of 860 nm decreased accompanying the formation of two new peaks at around 568 and 890 nm. The color of the polyamide 4e film changed drastically from nearly colorless to green (semioxidation stage), and finally to gray black (fully oxidation stage). Thus, the incorporation of DPA-MeF group to both of the diamine and dicarboxylic acid components endowed the resulting polyamide with multicolored electrochromic characteristic.

Optical switching studies were carried out to investigate the electrochromic properties more deeply with the transmittance monitored at the given wavelength as a function of time by stepping potential between neutral and oxidation states. The typical switching behavior of polyamide 4d was conducted by applying squarewave potential between 0 and 1.3 V and depicted in Figure 9. After 100 cycles, no obvious spectral decay was observed, indicating the highly stable electrochomic properties. The switching time is also an important parameter for electrochromic materials, and here, it was calculated as the time when the absorption intensity recovered to 90% of the full modulation. The polyamide 4d revealed a switching time of 5.4 s at 890 nm for the coloring process and 4.8 s for blenching process (Supporting Information Fig. S5). Coloration efficiency (CE) is also an important parameter for electrochromic materials, which was measured by monitoring the amount of ejected charge (Q) as a function of the change in optical density of the polymer films [CE = ΔOD/Qd, ΔOD = log (Tblenched/Tcolored)]. The CE could reach up to 216 cm² C⁻¹ at the first cycle and retained about 94% after 100 cycles (Supporting Information Table S1). Moreover, other polyamides exhibited similar electrochromic behavior, which indicates that these synthesized...
polyamides with DPA-MeF groups would be promising electrochromic materials.

**Electrofluorescent Properties**

In light of the enhanced fluorescence as well as stable electrochromic progress, the electrofluorescent switching of these polyamides were also examined through a measurement setup as shown in Figure 10(a). TPA\(^+\) is known as an effective fluorescence quencher\(^42\) and thus the fluorescence of the polyamides containing DPA-MeF group could be readily driven by electricity. As shown in Figure 10(b), the polyamide 4d film was excited at 360 nm and the emission spectra under applied potential were collected in the range of 380–660 nm. In the neutral state, the polymer film exhibited vivid blue-green fluorescence. After applied potential increasing from 0 to 1.3 V, the intensity of fluorescence became weaker and finally quenched to dark. The electrofluorescent film revealed a high contrast of 221.4. In addition, no shift of the spectral band was observed during the changes of fluorescence intensity, which indicates that the fluorescence quenching should be due to the electrochemical oxidation of DPA to DPA\(^+\) rather than the byproduct from secondary reaction. Furthermore, the stability and reversibility of the fluorescence switching was also investigated by repeatedly performing on-off cycles (0–1.3 V). The fluorescence switching operation was reversible, which could be repeated 10 times without noticeable fluorescence changes in both “on” and “off” states (Supporting Information Fig. S6). Thus, these stable and high-contrast electrochromic/electrofluorescent polyamides will actively promote the development of dual-switch display materials in the near future.

**CONCLUSIONS**

In summary, a series of polyamides with DPA-MeF group were prepared from condensation polymerization reactions of \(N,N\)-di(4-carboxyphenyl)-2-amino-9,9-dimethylfluorene and five diamines. These polyamides showed excellent solubility, good thermal properties, and interesting spectroscopic properties. Their enhanced fluorescence properties were observed in both solution and film states, which was investigated in detail by using TD-DFT method. Furthermore, the apparent color and fluorescence of these polyamides could be modulated reversibly and stably by electrochemical redox with a high-contrast. Thus, the reported properties prove that the multifunctional polyamides will contribute to the development of electrochromic/electrofluorescent dual-switching display in the future. Further studies on the stimuli-responsive aspects of these materials for flexible devices are currently carried out in our laboratories.

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