

Electrochromic and electroluminescent devices based on a novel branched quasi-dendritic fluorene-carbazole-2,5-bis(2-thienyl)-1*H*-pyrrole system†

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We report here the synthesis of a novel branched quasi-dendritic system, 9,9'-(9,9'-dihexylfluorene-2,7-diyl)bis[3,6-bis(2,5-bis(2-thienyl)pyrrol-1-yl)carbazole], (FCSNS), in four steps, followed by coating onto an ITO-coated glass surface by an electropolymerization process to give a very stable cross-linked polymeric film (poly-FCSNS). The yellowish-green color of this film in its neutral state changed reversibly to black upon oxidation. An electrochromic device, assembled in the sandwich configuration [ITO/anodically coloring polymer (poly-FCSNS)/gel electrolyte/cathodically coloring polymer (PEDOT)/ITO], exhibited a relatively short response time (about 1 s), a high redox stability, and a high coloration efficiency (1624 cm² C⁻¹). In addition to electrochromic studies, organic light-emitting diode (OLED) work was also carried out using FCSNS. A multilayer OLED having a configuration of ITO/PEDOT:PSS/FCSNS/Alq₃/LiF : Al was fabricated, and it showed a turn-on voltage of approximately 6 V and exhibited a bright green emission with a luminance of 3700 cd m⁻². The maximum luminous efficiency was found to be 2.0 cd A⁻¹ at 14 V and 11.75 mA cm⁻². The emitted light from the OLED device is green, and has the color coordinates of (x, y) (0.33, 0.54) according to CIE. Electrochemical and optical properties were also studied by using cyclic voltammetry, UV-Vis absorption and fluorescence spectroscopy, respectively.

Introduction

Charge transporting dendrimers, as a very special type of macromolecule with hyperbranched and perfectly defined structures, have attracted much attention for the opto-electronic device technologies such as organic light-emitting diodes (OLEDs),¹ field effect transistors (OFETs),² photovoltaic (PV) cells,³ and lasers.⁴ Over the last two decades there has been rapidly increasing interest in the field of conjugated dendrimers because they combine the advantages of both small molecules and polymers; for instance, the synthetic versatility of organic materials, the solubility of polymers in common solvents, and the ready achievement of a high purity of small molecules.⁵⁻⁸

Carbazole-based macromolecules have various advantages over other conjugated polymers as photonic materials.⁹

Carbazole is also easily functionalized at its 3,6-, 2,7- or *N*-positions,¹⁰ and can then be covalently linked into polymeric systems, both in the main chain as building blocks and in a side chain as pendant groups.¹¹ Many electron donor or acceptor groups are introduced along this backbone to form an alternative copolymer to tune the band-gap and other properties.¹² Furthermore, carbazole based macromolecules have been used in hole-transporting materials (HTMs) owing to their excellent hole-transporting capability, high charge carrier mobility, high thermal, morphological and photochemical stability.¹³ On the other hand, fluorene and its analogous derivatives, one of the blue luminescent materials with a wide energy gap and high luminescence efficiency, has drawn much attention from materials chemists and device physicists. One of the important applications of carbazole and fluorene derivatives is their use as HTMs in organic light-emitting diodes (OLEDs). It is known that fluorene derivatives are important materials for OLEDs because of their high quantum yield of photoluminescence (PL) and electroluminescence (EL) efficiencies as well as high thermal stabilities.¹⁴ 2,5-Bis-(2-thienyl)-1*H*-pyrrole¹⁵ (SNS) is one of the very important electroactive moieties for electrochromic applications for several reasons: (i) the oxidation potentials of the SNS derivatives are lower (about +0.7 V vs. SCE) than those

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of many of other electroactive materials, ii) the functionalization of the ter-heteroatom unit by the Knorr–Paal reaction seemed an attractive one step procedure for the introduction of various bridges into the monomer, iii) provided that good quality films can easily be generated on an ITO/glass surface by electropolymerization, high electrochromic performance would be obtained.¹⁶ Furthermore, it is coupled to the backbone of other electroactive or photoactive groups to tune their band-gaps and thus to gain useful properties.¹⁷

Electrochromism is observed in reversible redox systems which exhibit significant color changes by the effect of an applied potential.¹⁸ The color change generally occurs between a transparent and a colored state or between two colored states. This is effected by a small electric current at low potentials, of the order of a fraction of volts to a few volts.¹⁹ The first studies of electrochromic materials started with inorganic semiconductor materials such as tungsten trioxide and iridium dioxide, and then organic small molecules such as viologens and metallophthalocyanines.²⁰ Construction of small organic and inorganic molecules that contain multiple redox-active chromophores is fairly important for the preparation of novel polyelectrochromic materials, which respond to different potentials with a variety of colors.²¹

Since the electroluminescence from small molecular organic materials was reported for the first time in 1987 by Tang and Van Slyke,²² OLEDs have attracted much attention and found their way into markets as displays. Recent materials advances have enabled the concept of “plastic light” with the optical, electrical, and mechanical characteristics that render OLEDs truly disruptive technology within the display and lighting industries, since they are compatible with conventional device replacement and offer new opportunities for exploitation. With their advantages of low-power consumption, high contrast and high brightness, they have applications in full color flat panel displays.²³

In this paper, we report the synthesis and characterization of 9,9'-(9,9'-dihexylfluorene-2,7-diyl)bis[3,6-bis(2,5-bis(2-thienyl)pyrrol-1-yl)carbazole] (FCSNS) as a multipurpose material. An electropolymerization process was carried out to produce a cross-linked polymeric material (poly-FCSNS) *in situ* coated onto an ITO-glass surface, where it was then used to construct an electrochromic device. In order to

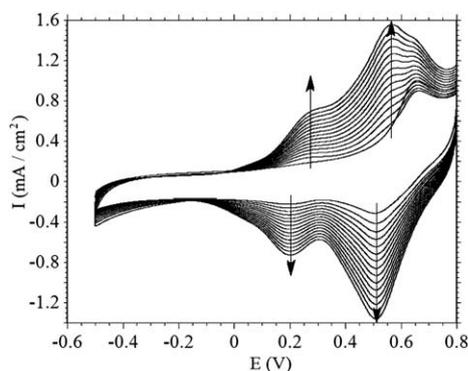


Fig. 1 Repeated potential scanning of FCSNS at a scan rate of 100 mV s⁻¹.

investigate the hole-transporting property of FCSNS, a multilayer OLED device was fabricated with a structure of ITO/PEDOT:PSS/FCSNS/Alq₃/LiF:Al, with Alq₃ acting as both the emissive layer (EML) and electron-transporting material (ETM).

Results and discussion

Synthesis and characterization

FCSNS was synthesized in four steps. First of all, 9,9'-(9,9'-dihexyl-9H-fluorene-2,7-diyl)bis-9H-carbazole (**1**) was synthesized according to the procedure published by Promarak *et al.*^{13a} The product **1** obtained from this reaction was then tetra-nitrated using an excess of Cu(NO₃)₂·2.5H₂O in a mixture of acetic acid and acetic anhydride (v/v, 1 : 2). The first and second reaction yields were found to be 67 and 75%, respectively. In the third step, the tetra-nitrated compound was reduced to the corresponding tetra-amine analogue by using palladium on activated carbon (Pd/C) and hydrazinium hydroxide (N₂H₅OH). Finally, the Paal–Knorr reaction was carried out between the tetra-amino compound and an excess of 1,4-di-2-thienylbutane-1,4-dione prepared from thiophene and succinyl chloride in dry toluene in presence of *p*-toluenesulfonic acid (PTSA) as the catalyst.¹⁵ The reaction yield of this last step was found to be 58%. The chemical structure of FCSNS was elucidated from its FT-IR, ¹H NMR, and MALDI-TOF data (see ESI†).

A cross-linking electropolymerization process was carried out in a reaction medium containing 2.0 × 10⁻³ M FCSNS and 0.1 M LiClO₄–NaClO₄ in a mixture of acetonitrile–dichloromethane (3 : 1; v/v) *via* repetitive cycling at a scan rate of 100 mV s⁻¹. Two new redox couples with half wave potentials (*E*) of 0.23 and 0.54 V were observed during the cyclic scans between –0.4 and +0.8 V and, after each successive cycle, the intensified oxidation waves clearly indicate the formation of cross-linked **poly-FCSNS** on the surface of working electrode (Fig. 1). After coating with **poly-FCSNS**, the ITO-glass surface was cleaned (*i.e.* dedoped) electrochemically in a monomer free-electrolyte solution in order to remove the residues. **Poly-FCSNS** was found to be very slightly soluble in dichloromethane by agitating in an ultrasonic bath. This solution was then used to measure the UV-Vis absorption spectrum of **poly-FCSNS**.

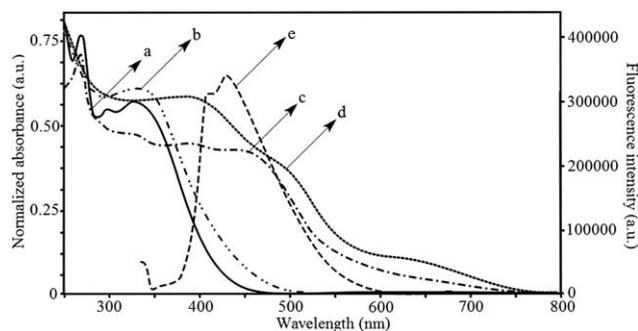
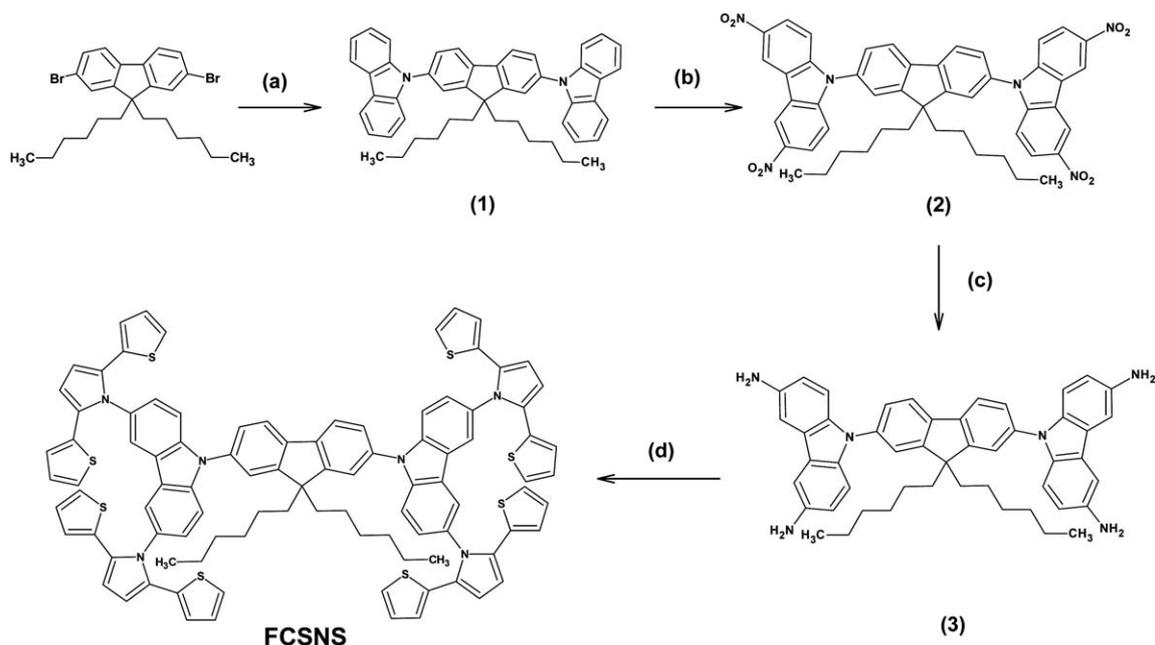


Fig. 2 UV-Vis absorption spectra of FCSNS in dichloromethane solution (a) and on the ITO-glass surface (b); **poly-FCSNS** in dichloromethane solution (c) and on the ITO-glass surface (d); emission spectra of FCSNS in dichloromethane solution (e).



Scheme 1 (a) Carbazole, Cu, K₂CO₃, nitrobenzene, 24h, reflux (b) acetic acid-acetic anhydride (1 : 2; v:v), Cu(NO₃)₂ × 2.5 H₂O, 24h, 80 °C (c) Pd/C, N₂H₅OH, EtOH, 24 h, reflux, (d) 1,4-dithiophene-2-yl-butane-1,4-dione, PTSA, toluene, reflux, 72 h.

Optical and electrochemical properties

The absorption spectra of **FCSNS** and **poly-FCSNS** were recorded in dichloromethane (liquid phase) and on the ITO-glass surface (solid phase) (Fig. 2). Due to having many photoactive groups in their structures, they showed multiple absorption bands attributed to π - π^* transitions of fluorene, carbazole and SNS moieties. In the liquid phase, while the maximum absorption band of **poly-FCSNS** is located at 332 nm, that of **poly-FCSNS** is broadened and showed a bathochromic shift. It is observed at 451 nm due to the extension of the conjugated system as a result of polymerization. The absorption behaviors were also investigated in the solid state, in which the well-known π -stacking interactions resulted in the broadening and red-shifting of the absorption bands of both the monomeric and polymeric materials. In the solid phase, the low energy onset of the **FCSNS** absorption band is shifted from 454 nm (equal to a band gap of 2.73 eV) to 622 nm (equal to a band gap of 1.99 eV) in **poly-FCSNS** upon cross-linking. A 168 nm red shift in the low energy onset induced by the process of polymerization can arise from the extended conjugation of the electroactive centers. In addition, the emission properties of **FCSNS** were also studied in the liquid phase. A strong emission band is found at 423 nm which corresponds to a blue color.

The electrochemical properties of **FCSNS** and **poly-FCSNS** were investigated by cyclic voltammetry. According to the voltammogram of **FCSNS** scanned in the anodic region, it shows three irreversible oxidation waves at 0.88, 1.58, 2.00 V (Fig. 3). The oxidation at 0.88 V is attributed to the SNS moiety, while the successive oxidations can be due to the other electroactive sites of **FCSNS**. Owing to the extended conjugation by cross-linking occurring between peripheral thiophenes, two reversible oxidation waves are observed at half wave potentials of 0.38 and 0.64 V; these values are lower than those of **FCSNS**. HOMO energy

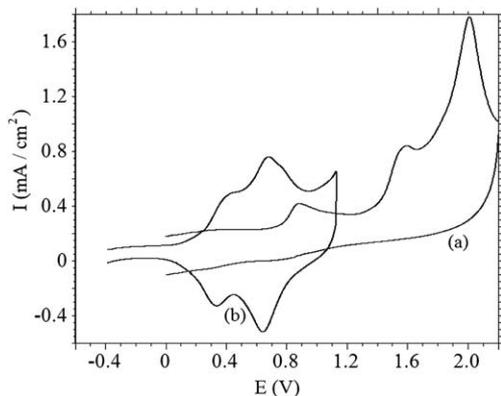


Fig. 3 CV of **FCSNS** (a) and **poly-FCSNS** (b) with a scan rate of 100 mV s⁻¹, vs. Ag/AgCl.

levels of **FCSNS** and **poly-FCSNS** were calculated by using the onset values of their oxidation potentials, and they are found to be -5.15 and -4.63 eV, respectively. Then, LUMO energy levels of the monomeric and polymeric materials were obtained by adding their optical band gap values to their HOMO levels, and they are calculated as -2.42 and -2.64 eV, respectively (Table 1).

From spectro-electrochemical measurements, both the electronic structure and optical behavior of **poly-FCSNS** on the transparent ITO-glass surface upon *p*-doping can be explained. During the scan from -0.4 to +0.8 V, the valence and conduction band (π - π^* transition) at about 445 nm initially decreased (< +0.4 V) and then a new band at 485 nm emerged at higher potentials (+0.4 V-+0.8 V). Furthermore, increased intensity of the broad band at about 880 nm indicates the formation of polarons and bipolarons on the **poly-FCSNS** structure (Fig. 4). Due to the presence of multiple electroactive moieties in the structure of **poly-FCSNS**, it absorbs from the visible (Vis) to the

Table 1 HOMO and LUMO energy levels and optical band gap (E_g) values of FCSNS and poly-FCSNS

Compounds	Oxidized groups and oxidation potentials/V		HOMO/eV	LUMO ^a /eV	E_g , Optical band gap/eV
	SNS	Carbazole and fluorene			
FCSNS	0.88 ^b 0.76 ^c	1.58 ^b and 2.00 ^b	-5.15	-2.42 ^a	2.73
poly-FCSNS	0.35 ^b -0.41 ^b reversible 0.61 ^b -0.67 ^b reversible 0.24 ^c	—	-4.63	-2.64 ^a	1.99

^a Calculated by the addition of the optical band gap to the HOMO level. ^b Peak potentials. ^c Onset potentials.

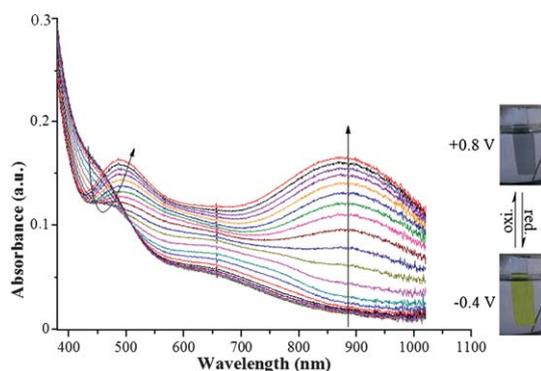


Fig. 4 Spectro-electrochemical measurements and color changes of the poly-FCSNS film.

near-infrared (NIR) region upon oxidation. Finally, the yellowish-green color of the film according to the color parameters of Commission Internationale de l'Eclairage (CIE) (luminance L : 75, hue a : -33, and saturation b : 67) turned black (L : 37; a : 5; b : -12) upon oxidation.

Electrochromic switching

Double step chronoamperometry was used to monitor the changes in the electro-optical responses during switching. Electrochromic parameters of the poly-FCSNS film were analyzed by the changes that occurred in the transmittance (increments and decrements of the absorbance band at 880 nm with respect to time) while switching the potential step wisely between neutral (-0.4 V) and oxidized states (+0.8 V) with a residence time of 10 s. During this process, the optical contrast value ($\Delta T\%$) of poly-FCSNS was found to be 21% (Fig. 5). Besides, the oxidation and reduction response times of this material were measured to be 1 and 2 s, respectively. The optical activity of the film was retained by 94.1% even after 5000 cycles of operation, indicating the high redox stability of the polymeric material. From the obtained results, it can be indicated that this material can be used in the construction and/or development of electrochromic devices and optical displays due to reversible redox behavior, low response time, and high resistance to overoxidation.

The coloration efficiency (CE) is an important parameter for electrochromic materials and this can be calculated by using $CE = \Delta OD/Q_d$ and $\Delta OD = \log(T_{\text{colored}}/T_{\text{bleached}})$, where Q_d is the injected/ejected charge between neutral and oxidized states,

T_{colored} and T_{bleached} are the transmittance in the oxidized and neutral states, respectively.²⁴ Using this equation, CE was measured to be 196 $\text{cm}^2 \text{C}^{-1}$ by chronoamperometry when the poly-FCSNS film on the ITO-glass surface was switched between -0.4 and 0.8 V. This value of CE is comparable to that obtained in related materials.^{16,17}

Spectro-electrochemistry of the poly-FCSNS/PEDOT electrochromic device (ECD)

During the coloration process, PEDOT and poly-FCSNS were reduced and oxidized, respectively. Figure 6 exhibits the spectro-electrochemical data of the poly-FCSNS/PEDOT device at voltages varying from -0.6 to 1.0 V. In the initial state (*i.e.* at -0.6 V), since the colors of the poly-FCSNS film and PEDOT film were yellowish-green and transparent blue, respectively, the color of the ECD became yellowish-green (L : 71; a : -31; b : 64). When this ECD was subjected to switching at higher potentials, such as between 0.0 and 1.0 V, due to the simultaneous reduction of PEDOT and oxidation of poly-FCSNS film, the peaks at 650 and 890 nm were intensified. Since the spectral signatures of both layers became dominant, the color of the device became dark blue (L : 1; a : 13; b : -26) (Fig. 6). The spectrum reveals that this device strongly absorbs between 450 and 1000 nm at the oxidized state. Because of this property, it can be used as a UV visible and NIR filter for various applications.

Switching of ECD

An electrochromic material is to be used in electrochromic displays and devices, it should have low response time (in order of a few seconds) and resistance to applied potential between its reduced and oxidized states. The change in optical transmission of the ECD was recorded at λ_{max} (650 and 890 nm) when it was switched at the potential between -0.6 and +1.0 V, with a residence time of 10 s. According to these measurements the response time from reduced to oxidized form and *vice versa* was found to be 1 s, which is the necessary time to complete 95% of the full optical switch. $\Delta T\%$ between the reduced (at -0.6 V) and oxidized (at +1.0 V) states were calculated as 42% for 650 nm and 28% for 890 nm, respectively (see Fig. 7). Besides, CE of the ECD was measured to be 1624 $\text{cm}^2 \text{C}^{-1}$. Cihaner and Algi reported the highest CE for the SNS-fluorene based electrochromic materials in the literature (25.600 $\text{cm}^2 \text{C}^{-1}$).^{17b} In addition; Cirpan *et al.*, reported that electrochromic devices based on

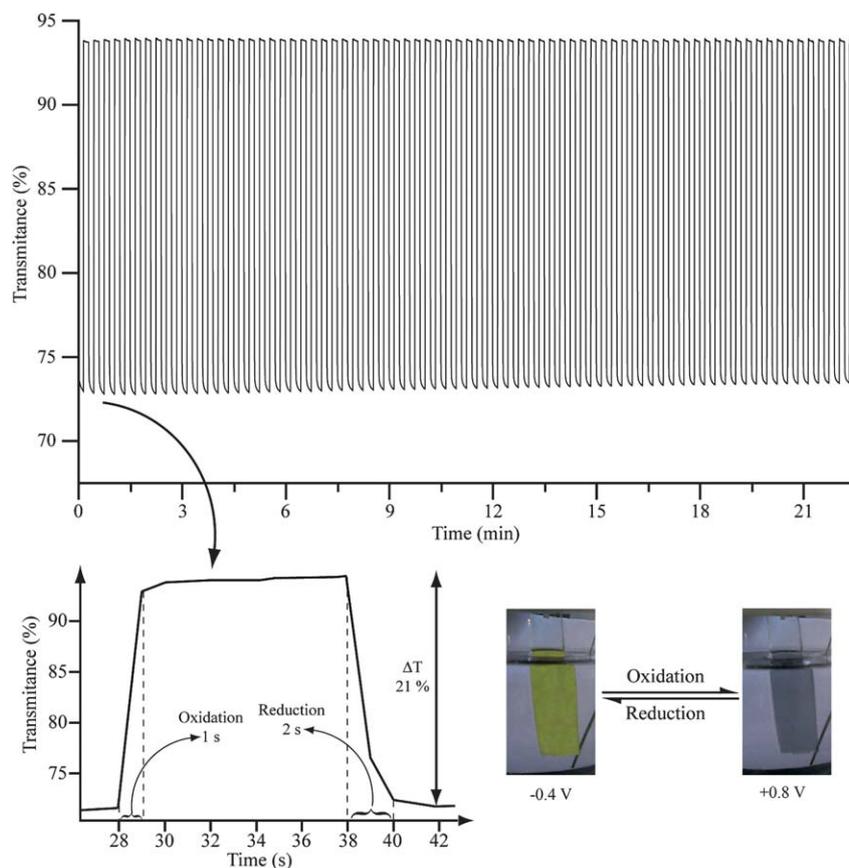


Fig. 5 Electrochromic switching, optical absorbance monitored for **poly-FCSNS** film at 880 nm (-0.4 – $+0.8$ V).

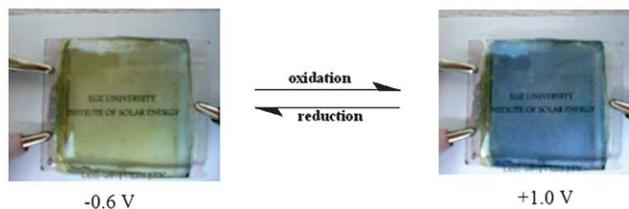
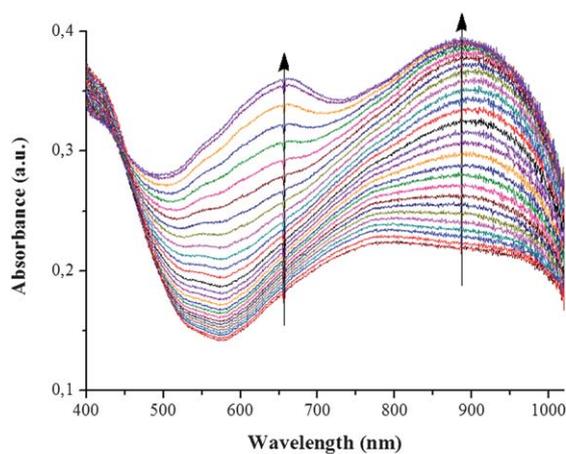


Fig. 6 Spectro-electrochemical measurements and the color changes of dual **poly-FCSNS/PEDOT** device.

EDOT-Carbazole-EDOT derivatives presents CE as $4804 \text{ cm}^2 \text{ C}^{-1}$.^{12e} However, other ECDs based on SNS derivatives presents lower values than that of synthesized **FCSNS** based device. As a consequence, this value of CE is one of the highest values in the literature.¹⁷ These electro-optical results also reveals that **poly-FCSNS** has a very strong redox response, since it retains its electrochromic activity even after 5000 switching cycles between reduced and oxidized states (98.7%) (Fig.7). This is a similar strong redox response behavior when compared to our previous study about based on SNS-carbazole derivative.^{17f} Finally, these behaviors make **poly-FCSNS** a superior material than the other previously reported SNS containing analogues^{16,17} because of its working range.

Electroluminescent properties

In order to investigate the effect of the hole-transporting properties of the **FCSNS** monomer on the device performance, an OLED device was fabricated with the structure of ITO/PEDOT:PSS/HTL(**FCSNS**)/Alq₃/LiF:Al (Fig. 8). Alq₃ was used as the EML and ETL, ITO as the anode and LiF:Al as the cathode. The EL spectrum of the device is shown in Figure 9. When a positive voltage was applied to the device, a bright green EL with a maximum around 528 nm was obtained. When the hole transport layer (HTL) materials have a planar molecular structure, the OLED device fabricated from such materials generally shows emission at longer wavelength due to the

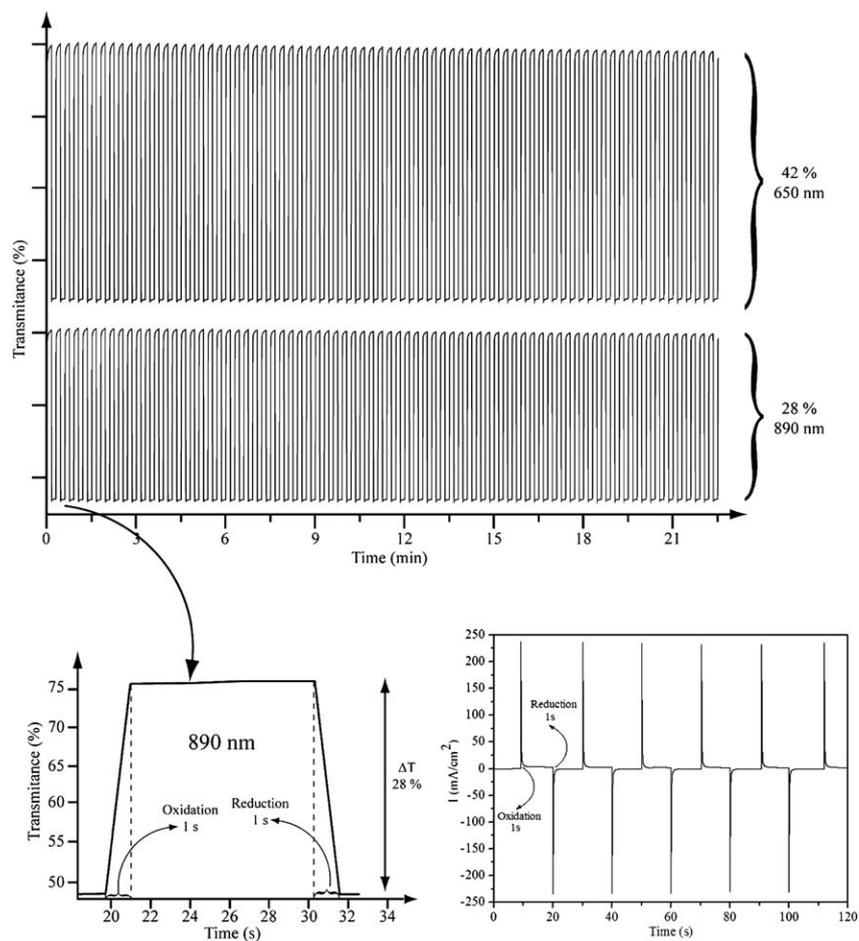


Fig. 7 Electrochromic switching, optical absorbance monitored for poly-FCSNS/PEDOT device at 650 and 890 nm (-0.6 – $+1.0$ V).

exciplex formation at the interface of HTL and ETL materials.¹³ Because of the nonplanar molecular structure of FCSNS, no emission was observed at longer wavelengths from the exciplex

species. The agreement between the EL spectrum of the fabricated device and the PL spectrum of Alq₃ show that the hole–electron recombination zone is well confined in the Alq₃ layer.

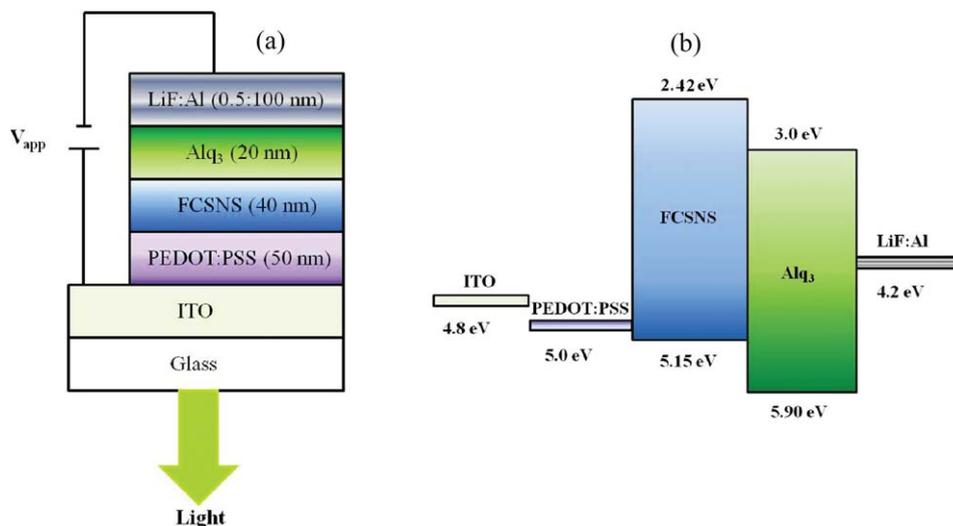


Fig. 8 a) Schematic illustration of ITO/PEDOT:PSS/FCSNS/Alq₃/LiF : Al OLED device. b) Energy band diagram of ITO/PEDOT:PSS/FCSNS/Alq₃/LiF : Al device.

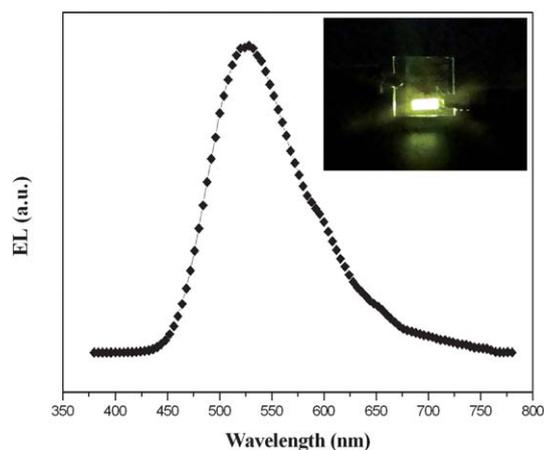


Fig. 9 EL spectrum of the ITO/PEDOT:PSS/FCSNS/Alq₃/LiF : Al device.

The color coordinate of this EL value according to CIE 1931 were measured as $(x, y) = (0.33, 0.54)$, which suggests that the device emits green light.

Figure 10 shows the current–voltage–luminance characteristics of the ITO/PEDOT:PSS/FCSNS/Alq₃/LiF : Al device. The electrical parameters obtained from this device are summarized in Table 2. From luminance–voltage characteristics, the device showed a turn-on voltage of 6 V and the maximum luminance of 3700 cd m⁻² was achieved at 20 V. The maximum luminous efficiency of the device was found to be 2.0 cd A⁻¹ at 11.75 mA

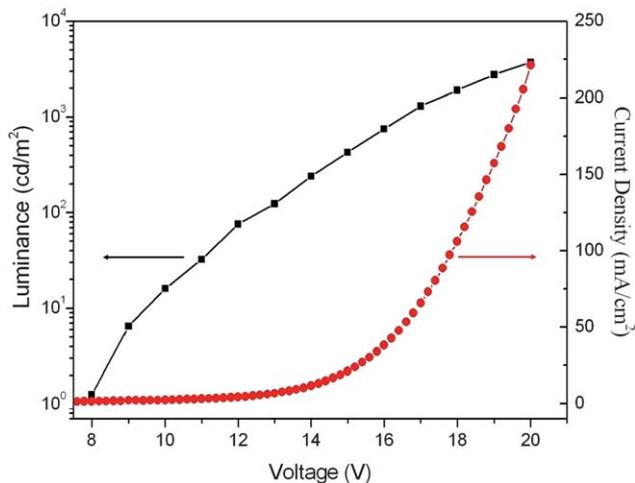


Fig. 10 Current density–applied voltage–luminance characteristics of the ITO/PEDOT:PSS/FCSNS/Alq₃/LiF : Al device.

Table 2 The electrical parameters of the OLED device

Device	Turn-on voltage/V	λ_{EL}/nm	Maximum Luminance/cd m ⁻²	CIE _X	CIE _Y	Maximum EL efficiency/cd A ⁻¹
ITO/PEDOT:PSS/FCSNS/Alq ₃ /LiF : Al	6	528	3700	0.33	0.54	2.0
ITO/PEDOT:PSS/Alq ₃ /LiF : Al	5	520	700	0.31	0.51	0.5
ITO/PEDOT:PSS/TPD/Alq ₃ /LiF : Al ²⁵	3	520	1760	—	—	8.2

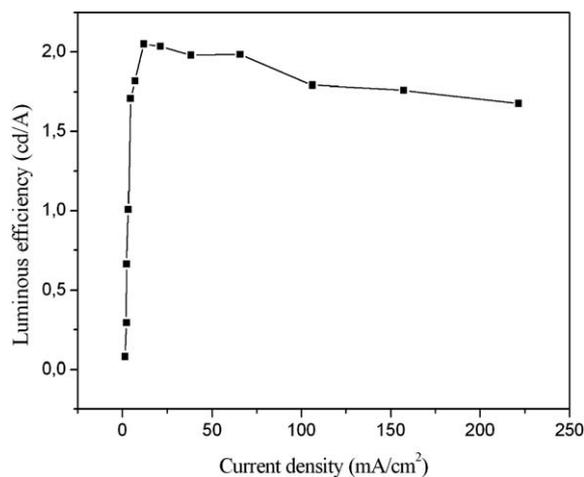


Fig. 11 The luminous efficiency–current density characteristics of the ITO/PEDOT:PSS/FCSNS/Alq₃/LiF : Al device.

cm⁻² from its luminous efficiency–current density characteristics as depicted in Figure 11. When the current density was increased from 11.75 mA cm⁻² to 221 mA cm⁻², the luminous efficiency showed only a mild decrease (0.38 cd A⁻¹).

Mu *et al.* investigated the performance of OLED devices with Alq₃/TPD active regions using various anode and cathode electrode structures.²⁵ They achieved the best performance from an OLED device with a configuration of ITO/PEDOT:PSS (50 nm)/TPD (50 nm)/Alq₃ (40 nm)/LiF : Al (1 : 100 nm). The electrical parameters obtained from this OLED device are summarized in Table 2. They reported a maximum luminance of 1720 cd m⁻² at 25 V, a turn-on voltage of 3 V and EL efficiency of 8.2 cd A⁻¹ at a brightness of 100 cd m⁻² and 5 V. When these results are compared with this present study, although the turn-on voltage of the OLED based on FCSNS is higher, our device shows higher brightness (3700 cd m⁻²) at lower voltage (20 V) than device with TPD molecule.

In our previous study, we described hole-transporting properties of several fluorene carbazole dendrimers in multilayer OLED devices with Alq₃ as ELT and ETL materials.^{13c} The OLED device based on spiro functionalized cores containing thiophene units at their peripheral carbazole dendrons as HTL material (**SFCT-G2**) showed maximum performance and exhibited bright green emission with a peak centered at 516 nm. The maximum luminance and luminous efficiency of this device were obtained as 25400 cd m⁻² and 7.7 cd A⁻¹, respectively. The devices containing **SFCT-G2** have much better performance in terms of brightness, current density and current efficiency than the others. In this present study, the device with FCSNS molecule

as HTL showed lower luminance and luminous efficiency, because of the inefficient hole transporting property as a result of intense interaction of the electroactive groups present on the fluorene core functionalized with linear alkyl chains. However, replacement of linear alkyl chains by a cyclic isomer bonded to fluorene in a spiro fashion creates a more pronounced 3D on the molecule. Due to this property of the molecule, there should be less interaction which means a better HTL functionality. Besides, the reference device based on ITO/PEDOT:PSS/Alq₃/LiF : Al was fabricated to evaluate interfacial layer in the hole injection properties (Table 2). The FCSNS layer improved the luminance and current efficiency of standard ITO/PEDOT:PSS/Alq₃/LiF : Al device.

Experimental

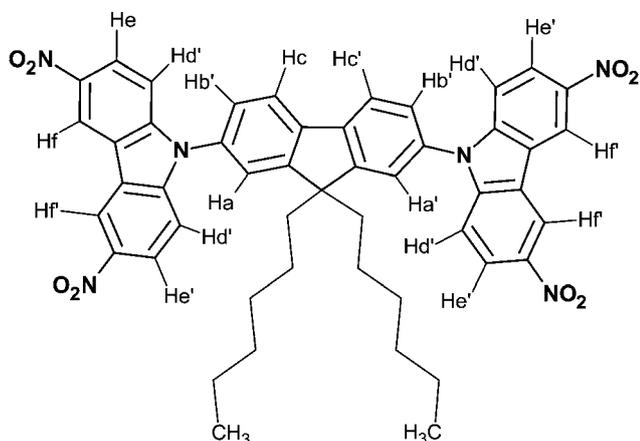
Materials

All chemicals were purchased from Aldrich and Fluka and used without further purification. 1,4-dithiophene-2-yl-butane-1,4-dione were prepared from previously published procedures.²⁶ Further, the synthesis and the characterizations of 9,9'-(9,9'-dihexylfluorene-2,7-diyl)dicarbazole (**1**) was previously described by Promarak *et al.*¹³

Synthesis of 9,9'-(9,9'-dihexylfluorene-2,7-diyl)bis(3,6-dinitrocarbazole) (**2**)

Cu(NO₃)₂·2.5H₂O (3.5 g, 15 mmol) was added into a mixture of acetic acid (15 mL) and acetic anhydride (30 mL) at room temperature. The mixture was stirred for 10 min, and then **1** (1.33 g, 2 mmol) was slowly added to this solution. After 5 min, 10 mL acetic acid was added to the reaction mixture. The mixture was further stirred at 80 °C for 24 h and then poured into ice water (500 mL). The yellow precipitate was collected by filtration, washed with water (3 × 300 mL) and dried at 60 °C under vacuum. mp: 299 °C, *yield*: 1.27 g, 75%.

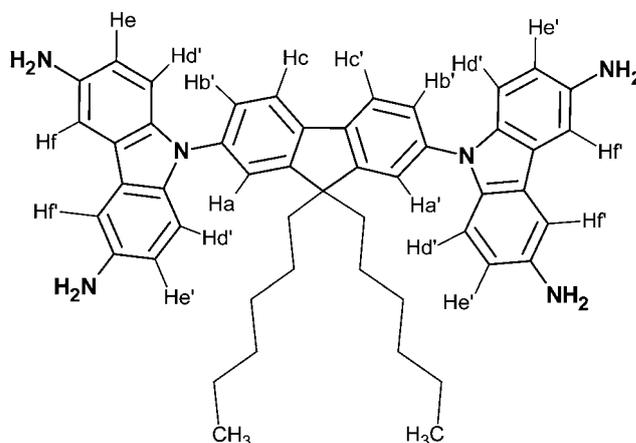
UV-Vis (λ_{max}) (CHCl₃): 265, 292 and 365 nm. FT-IR (cm⁻¹) 3090, 3048 (C-H aromatic); 2925, 2875 (C-H aliphatic) 1603, 1480 (C=C phenyl) 1511, 1329 (-NO₂); ¹H-NMR (CHCl₃-d): ppm, 9.25 (s, 4H, Ar-H_{ff'}); 8.5 (d, 4H, Ar-H_{ee'}); 8.15 (d, 2H, Ar-H_{cc'}); 7.68 (d, 2H, Ar-H_{bb'}); 7.65 (s, 2H, Ar-H_{aa'}); 7.5 (d, 4H, Ar-H_{dd'}); 2.13–0.84 (m, 26 H, C-H aliphatic).



Synthesis of 9,9'-(9,9'-dihexylfluorene-2,7-diyl)bis(3,6-diaminocarbazole) (**3**)

Pd/C (10%, w/w) (0.01 g) was added to the solution of **2** (1.27 g; 1.5 mmol) in 150 mL ethanol at room temperature. Then the mixture was heated to reflux temperature for 10 min. 10 mL of hydraziniumhydroxide (N₂H₅OH) in 30 mL ethanol was then added to the solution dropwise for 45 min. The mixture was stirred at 80 °C for 24 h and then the Pd/C was filtered off. Ethanol was removed by rotary evaporation and remaining solid was crystallized from toluene twice. The solid was dried at 50 °C under vacuum. mp: 157 °C, *yield*: 0.95 g, 86%.

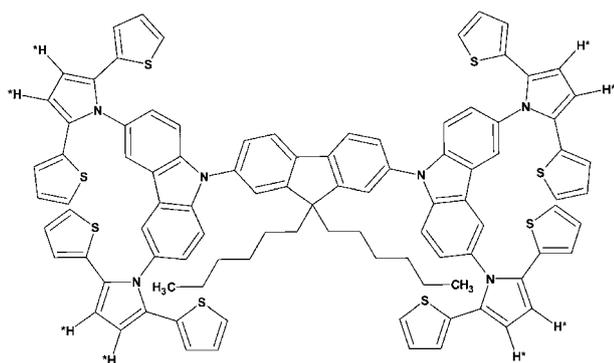
UV-Vis (λ_{max})(CHC₃): 294, 340 nm; FT-IR (cm⁻¹) 3418, 3336 (-NH₂); 3058 (C-H aromatic); 2924, 2871, (C-H aliphatic); 1610, 1579, 1491 (C=C phenyl); ¹H-NMR (CHCl₃-d): ppm, 7.92 (d, 2H, Ar-H_{cc'}); 7.57 (d, 2H, Ar-H_{bb'}); 7.54 (s, 2H, Ar-H_{aa'}); 7.4 (d, 4H, Ar-H_{ff'}); 7.23 (d, 4H, Ar-H_{dd'}); 6.8 (d, 4H, Ar-H_{ee'}); 3.4 (broad, 2H, -NH₂) 2.13–0.84 (m, 26 H, C-H aliphatic).



Synthesis of 9,9'-(9,9'-dihexyl-9H-fluorene-2,7-diyl)bis[3,6-bis(2,5-di-2-thienyl-1H-pyrrol-1-yl)-9H-carbazole] (FCSNS, Scheme 1)

3 (0.75 g, 1 mmol), 1,4-Dithiophene-2-yl-butane-1,4-dione, (2 g, 8 mmol), and *p*-toluenesulfonic acid (27 mg, 1 mmol) in 80 mL dry toluene were heated under reflux in a Dean-Stark apparatus until all the starting materials were consumed. The reaction was controlled by thin layer chromatography. After 72h, the mixture was cooled and poured into cold ethanol (500 mL). The yellow precipitate was collected by filtration, and the residue was purified by column chromatography (silica gel, 2 : 1 CHCl₃-hexane). mp: 61 °C *yield*: 0.65 g, 41%.

UV-Vis (λ_{max}),(CHCl₃, nm): 264 298 and 332, FT-IR (cm⁻¹): 3096; 3071, 3044, (C-H aromatic); 2924, 2871 (C-H aliphatic); 1602,1512, 1491, (C=C); ¹H-NMR (CHCl₃-d, ppm): δ 8.03–6.59, (m, 42H, C-H aromatic); 6.55, (s, 8H, Ar-H*); 2.13–0.73 (m, 26 H, C-H aliphatic); MALDI-TOF (*m/z*): [M⁺] calcd. for C₉₇H₇₆N₆S₈, 1580.39; found, 1580.33.



Electrochemical polymerization (poly-FCSNS)

Cross-linked electrochemical polymerization of **FCSNS** were performed in a reaction medium containing 2×10^{-3} M monomer and 0.1 M TBAPF₆ in acetonitrile–dichloromethane (3 : 1, v:v) solution *via* repetitive cycling at a scan rate of 100 mV s⁻¹. A platinum wire was used as a counter electrode and Ag wire as a reference. The polymer was coated onto platinum wire (0.02 cm²) or ITO (8–12 Ω, 0.8 cm × 5 cm). The active area of coated polymer on ITO was adjusted to 1 cm². Finally, the film was rinsed with acetonitrile to remove electrolyte salt.

Instrumentation

FT-IR spectra were recorded by a Perkin Elmer FT-IR Spectrum One by using ATR system (4000–650 cm⁻¹). ¹H NMR and ¹³C NMR (Bruker Avance DPX-400) spectra were recorded at 25 °C in deuterated chloroform and TMS as internal standard. MALDI-TOF spectra of the material were recorded by an Applied Biosystems Voyager System 6020 instrument.

Cyclic voltammetry (CV), used for electrochemical measurements was performed using a CHI660B electrochemical workstation from CH Instruments (Austin, TX, USA). CV measurements were carried under an argon atmosphere and the electrochemical cell includes an Ag/AgCl as reference electrode (RE), Pt wire as counter electrode (CE) and glassy carbon as working electrode (WE) immersed in 0.1 M TBAPF₆ as the supporting electrolyte. HOMO and LUMO energy levels of the polymer were calculated according to the inner reference ferrocene redox couple $E^{\circ}(\text{Fc}/\text{Fc}^+) = +0.41$ V (vs. Ag/AgCl) in acetonitrile by using the formula $E_{\text{HOMO}} = -e(E_{\text{ox}} - E_{\text{Fc}}) + (-4.8 \text{ eV})$.²⁷ Onset values of oxidation potentials were taken into account while calculating HOMO energy levels. LUMO energy levels were calculated by addition of the optical band gap to the HOMO level.

UV-Vis spectra were recorded by Analytic Jena Speedcord S-600 diode-array spectrophotometer. The absorption spectra of monomer and polymer were recorded in dichloromethane (liquid phase) and on ITO-glass transparent film (solid phase). The optical band gap (E_g) of products were calculated from their low energy absorption edges (λ_{onset}) ($E_g = 1241/\lambda_{\text{onset}}$).²⁸

The data obtained from UV-Vis spectra and cyclic voltammetry were used for spectro-electrochemical measurements of **poly-FCSNS** on an ITO-glass transparent film.²⁹ The measurements were carried out to consider absorption spectra of this polymer film under applied voltage. The spectro-electrochemical

cell consisted of a quartz cell, an Ag wire (RE), Pt wire counter electrode (CE) and ITO/glass as transparent working electrode (WE). Measurements were carried out in 0.1 M TBAPF₆ as the supporting electrolyte in acetonitrile.

Colorimetry measurements were performed using a Konica Minolta CS-200 chromameter with viewing geometry as recommended by CIE. According to the CIE system, the color is made up of three attributes; luminance (L), hue (a), and saturation (b). These parameters were measured at neutral, intermediate and fully oxidized states of the electrochromic polymer on the ITO-glass surface.

Fabrication of ECD

For a dual type electrochromic device (ECD) fabrication, PEDOT was deposited electrochemically onto a 20 cm² ITO-glass surface from an acetonitrile solution containing 2×10^{-3} M PEDOT and 0.1 M TBAPF₆ by applying static voltage at 1.2 V. A platinum wire was used as a counter electrode and Ag wire as a reference. After coating the electroactive material onto the ITO-glass surface *via* electro-oxidative polymerization, the film was rinsed with acetonitrile. A gel electrolyte prepared from LiClO₄/ACN/PMMA/PC in the ratio of 3 : 70 : 7 : 20 by weight was used as conducting layer between anodically and cathodically conducting polymer layers in the ECD. Just after dissolution of LiClO₄ in acetonitrile, poly(methylmethacrylate) (PMMA) was plasticized by adding 1,2-propylenecarbonate (PC) in order to form a highly transparent and conductive gel.³⁰ ECD was prepared in three steps: In the first step, two electrochromic layers—a cathodically coloring polymer (PEDOT) and an anodically coloring polymer (**poly-FCSNS**)—were deposited onto individual transparent ITO-glass surfaces. Then, in the second step, a gel electrolyte was spread over the face of each layer. Finally individual ITO-glass layers were stacked face-to-face.³⁰

Fabrication and characterization of OLED

Indium tin oxide (ITO) glass substrate with a sheet resistance 15Ω/□ was used. After etching ITO and cleaning in an ultrasonic bath with acetone and iso-propanol according to standard cleaning procedures, the active area of 10 mm² was obtained. PEDOT:PSS was spin-coated onto the substrate at a spin speed of 4000 rpm for 30 s forming a 50 nm thick layer. The samples were annealed under a nitrogen atmosphere for 30 min at 150 °C. Thin films of **FCSNS** as HTL with a thickness of 40 nm was obtained by spin-coating from its chlorobenzene solution with a concentration of 1.5% w/v onto ITO-glass substrates at a spin speed of 3000 rpm for 30 s. Then Alq₃ was deposited onto the surface of the **FCSNS** film as EML and ETL with a thickness of 20 nm. Finally, an ultra-thin LiF layer (0.5 nm) and Al cathode (100 nm) were coated by vapor deposition. The characterization was carried out under an inert nitrogen environment inside a glove box system. A Keithley 236 source meter was used to investigate I - V characteristics. The EL and luminance properties were measured using a Spectrascan PR-655 spectroradiometer.

Conclusion

Herein, we reported the synthesis of a novel electroactive branched quasi-dendritic system containing a fluorene-carbazole-SNS moiety. FT-IR, ¹H NMR and MALDI-TOF results were used for the structural characterization. Poly-FCSNS was coated on to an ITO-glass surface by using a cross-linked electrochemical polymerization process to give a very stable electrochromic film. The yellowish-green color of the film in the neutral state changed reversibly to black upon oxidation. Furthermore, an electrochromic device was also assembled from poly-FCSNS in the sandwich configuration, ITO/poly-FCSNS//gel electrolyte/PEDOT/ITO. The color of the constructed device switched between yellowish-green and dark blue upon the application of potential between -0.6 and +1.0 V. Further, the oxidation and reduction response time of the electrochromic device were found to be relatively low and the optical activity of the device is very high even after thousands of cycles. As a result, this electrochromic device exhibits reversible electrochemical oxidation, low driving voltage, high CE and high redox stability. Furthermore this device strongly absorbs in the visible and NIR region in the oxidized state, and could therefore be used as a visible and NIR filter for various applications.

In the second part of the study, a multilayer OLED device having the configuration of ITO/PEDOT:PSS/FCSNS/Alq₃/LiF:Al was constructed and it showed a turn-on voltage of approximately 6 V and exhibited a bright green emission with a maximum luminance of 3700 cd m⁻². The maximum luminance efficiency was found to be 2 cd A⁻¹ at 14 V and 11.75 mA cm⁻². The CIE coordinates were measured as (0.33, 0.54), which suggested that the device can emit a green light. Further, FCSNS can be used as a multipurpose material that will receive a great deal of the attention from opto-electronic technologies.

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