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Investigation Of Improvement In Electrochemical Stability Of PEDOT Based Copolymer By Star-Like Copolymerization On Carbazole-POSS Moiety

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Abstract

Due to their stability and reversible redox activity, PEDOT-based copolymers are extensively investigated for electrochromic applications. For that reason, different modifications have been tried on the structure of PEDOT polymer in order to control both electrochemical and optical characteristics. Copolymerization of EDOT with carbazole monomer is one of the used modifications to alter and improve electrochromic properties. Despite these modifications, the electrochemical stability of the PEDOT-based copolymers is still a debate. To this end, a star-like shape of poly (EDOT-co-OctaCBz-POSS) copolymer was electrochemically synthesized by incorporating a carbazole-substituted polyhedral oligomeric silsesquioxane (OctaCBz-POSS) nanostructure unit into the 3,4-ethylenedioxythiophene (EDOT) backbone. The electrochemical behavior of the copolymer was investigated through cyclic voltammetry (CV) and stability tests, while the spectro-electrochemical properties were characterized using UV spectroscopy, chronoabsorptometry, and CIE Lab colorimetry. The copolymer shows a band gap (~1.88 eV) and a reduced onset oxidation potential compared to PEDOT, suggesting that the electron-donating OctaCBz-POSS enhances charge injection. The electrochemical stability of the copolymer retains about 25% after 120 cycles, whereas PEDOT loses its electroactivity after 60 cycles. UV-Vis spectroscopy indicates a slight hypsochromic shift compared to PEDOT, and chronoabsorptometry demonstrates good coloration efficiency (~245 at 570 nm), and rapid switching (~1.0 s). Upon applying a potential, the copolymer exhibited a wide range of colors, from deep purple (L ~22, a* ~21, b* ~41) at -1.0 V to blue-gray (L* ~59, a* ~-10, b* ~-19) at 1.5 V, depending on the applied voltage.*

Keywords*: 3,4-ethylenedioxythiophene (EDOT), Carbazole, polyhedral oligomeric silsesquioxane (OctaCBz-POSS), PEDOT, Copolymer, electropolymerization.*

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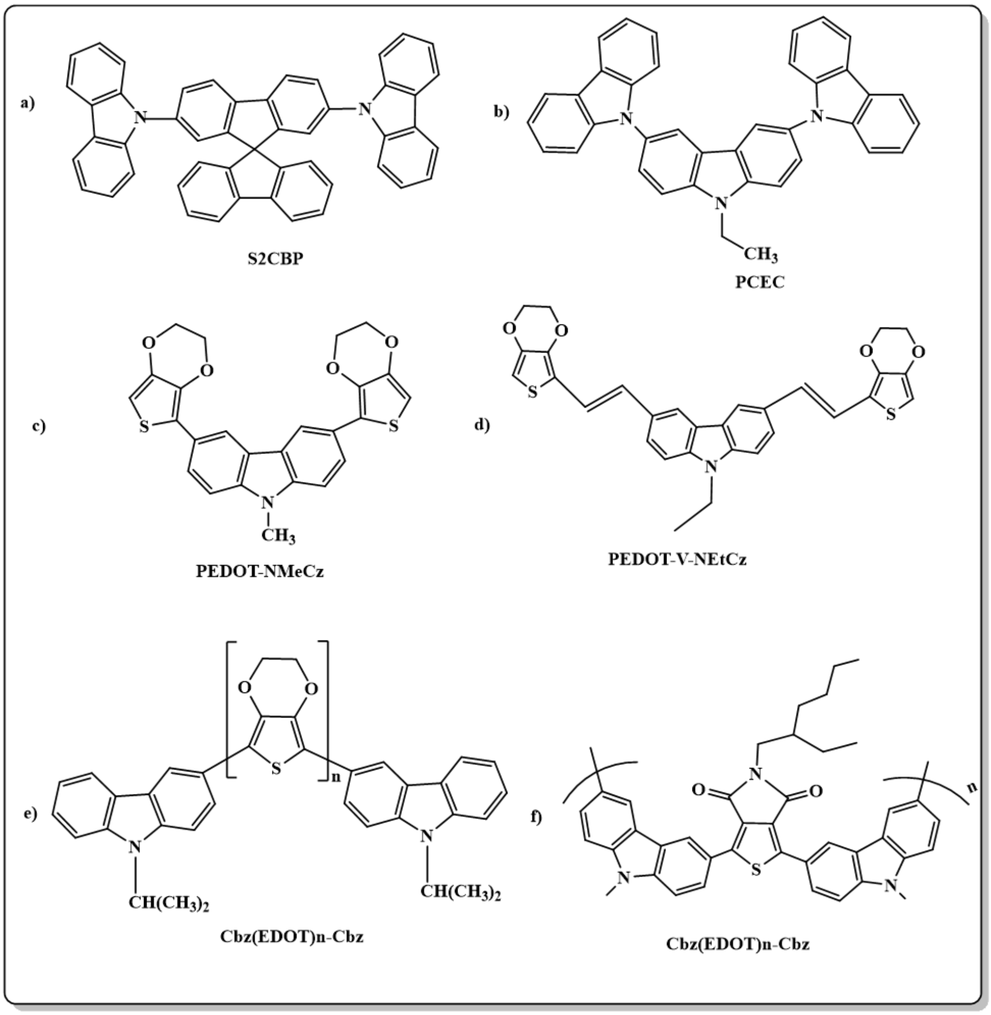
I. Introduction

Electrochromic materials, which offer reversible color alterations under applied electrochemical potentials, are leading advancements in next-generation optoelectronic technologies, such as smart windows [1], flexible displays [2], wearable electronics [3], and adaptive camouflage [4]. Various materials exhibit this characteristic, including transition metal oxides, metal-coordinated complexes, organic molecules, and conducting polymers. Conducting polymers are distinguished in this field due to their adjustable bandgap, rapid switching kinetics, and economical production [5]. Moreover, conducting polymers in smart windows improves energy efficiency and functionality in architectural settings. These materials offer unique properties such as tunable optical characteristics, electrochemical stability, mechanical flexibility, the ability to modulate light transmittance, and the versatility of color changes [6]. The electrochromic characteristics of these polymers, influenced by their molecular structures- including conjugation length, side chains, donor-acceptor interactions, and building blocks- affect the electrochromic performance of π-π conjugated polymers, facilitating vibrant color transitions and enhancing their overall performance[7]. In this regard, Beaujuge et al. reviewed the fundamentals of polymer electrochromism and demonstrated that alterations in chemical structure facilitate vibrant color shifts. The review details strategies for tuning polymer band gaps and colors through molecular design and highlighting their ability to achieve diverse color states (e.g., red, blue, green, and yellow) for multicolored electrochromic polymers (e.g., polythiophenes, polydioxythiophenes, and polyfluorenes). However, they mentioned that ensuring durability during repeated redox cycling is difficult, as degradation from irreversible redox reactions can reduce contrast and device lifespan [8]. Within these polymers, carbazole-based polymers stand out in electrochromic applications owing to their unique blending of electrical, optical, and mechanical properties and practical fabrication advantages. They also demonstrate exceptional hole-transport characteristics, making them viable options for electrochromic devices [9]. For instance, Su Y et al. found that polycarbazole exhibits high optical contrast (ΔT) between the reduced state ($T_{red)}$ and oxidized state (T_{ox}) [10]. The study showed that polycarbazole derivatives, such as poly(2,7-bis(carbazol-9-yl)-9,9-spirobifluorene) (PS2CBP) (a), and poly(3,6-bis(N-carbazole)-N-ethylcarbazole) (PCEC) (b), exhibit reversible multicolor transitions comprising four distinct colors: gray at 0 V, grayish green at 1.0 V, and moss green. They also exhibit significant optical contrast (38.25% at 586 nm) and elevated coloration efficiency (369.85 $cm^2\ C^{-1}$ at 586 nm).

Unlike homopolymers, copolymers allow fine-tuning of optical and electronic properties, making them ideal for advanced electrochromic devices (ECDs) such as smart windows, displays, and anti-glare mirrors. The electrochromic properties that can be enhanced by copolymerization are color tunability (multi-color switching), optical contrast, switching speed, stability and working potentials. Therefore, it can be concluded that electrochromic copolymers can outperform homopolymers by enabling customizable colors, faster switching, and longer lifetimes, driving innovations in energy-efficient smart glass, wearable tech, and stealth materials[11][12][13][11], [12], [13], [14]. However, their limited conductivity, stability, and optical contrast often necessitate copolymerization with electron-rich units such as Fluorene [15], benzothiadiazole[16], pyrrole [17], and ethylene dioxythiophene (EDOT) [18] to enhance electrochromic performance. Among these units, (EDOT) has received a significant attention in copolymerizing with carbazole because it is a highly stable, also its copolymers attain low band gaps, elevated coloration efficiencies, and dynamic multichromatic behavior, exceeding the constraints of their homopolymer equivalents [5]. For instance, Reynolds et al. prepared a copolymer of 3,6-bis(2-(3,4-ethylenedioxy) thienyl)-*N*-methylcarbazole (BEDOT−*N*MeCz) (c) electrochemically; this copolymer exhibits low band gaps (1.8 eV), elevated coloration efficiency (up to 258 cm^2/C at 900 nm), and vivid multichromic properties, facilitating its use in high-contrast electrochromic devices (ECDs)[19]. Moreover, Wang et al. worked on the synthesis and characterization of a novel electrochromic polymer N-ethyl-3,6-Bis[(E)-2-(3,4-ethylenedioxythien-2-yl) vin-1yl]carbazole PBEDOT-V-NEtCz (d), which is generated from a vinylene-linked monomer (BEDOT-V-NEtCz) that combines 3,4-ethylenedioxythiophene (EDOT) and N-ethyl-carbazole (NEtCz). Spectroelectrochemical analysis revealed vibrant multicolor transitions ranging from brick-red, brown, olive green, and blue-green, to blue, with a low optical band gap of 1.77 eV. It demonstrated excellent electrochemical stability, making it promising for applications in displays and smart windows [20]. From another aspect, Z. El Maliki et al., synthesized Cbz(EDOT)n-Cbz (e) and they found that the optical and electrical characteristics of EDOT-carbazole copolymers are enhanced by increasing chain lengths due to a reduction in band gap and an increase in absorption wavelengths (λ max). Additionally, the copolymers exhibit strong p-electron delocalization, which enhances hole injection and significantly modulates the electronic and optical characteristics, making them suitable for various optoelectronic applications [21]. Furthermore, M. Akbayrak, reported the synthesis of a new carbazole derivative, 5-(2-ethylhexyl)-1,3-bis(9-methyl-9H-carbazol-3-yl)-5H-thieno[3,4-c] pyrrole-4,6-dione (f), bearing a strong acceptor unit, and its electrochemical copolymerization with EDOT. The EDOT-carbazole copolymers demonstrate reduced optical bandgap values relative to the CzPDICz homopolymer, exhibiting values like those of PEDOT. The copolymers show a blue color in their neutral state and a transparent green in the oxidized state. Electrical properties reveal a non-diffusional redox process with well-adhering films. Increasing the CzPDICz ratio in the copolymer affects both the optical absorption spectra and the onset oxidation potentials, indicating a tunable electro-optical behavior based on molecular structure [22]. Recently, Carbas et al., indicated that poly(carbazole-co-EDOT) possesses a coloration efficiency of 192 cm^2/C at 745 nm and a band gap of 1.74 eV, while demonstrating multielectrochromic properties, highlighting its suitability for high-contrast electrochromic devices (ECDs)[23]. Moreover, Xu et al. emphasized their capability for black-to-transmissive transition, an essential attribute for smart window applications. This article delves into the synthesis, electrochromic mechanisms, and applications of carbazole-EDOT copolymers. It addresses challenges such as cyclic stability and scalability and explores future directions for their integration into advanced optoelectronic systems [24].



Scheme 1. Carbazole and Carbazole-EDOT based compounds and their copolymers in literature.

As the research related to improving the electrochromic properties of these copolymers increased, the researchers focused on enhancing their redox stability. Hayashi found that copolymers with greater molecular weights demonstrate improved electrochemical stability. For instance, a copolymer with a molecular weight of 70200 g/mol retained 65% of its charge storage capacity after 100 scans, compared to only 25% for a lower molecular weight variant. Additionally, the stability is attributed to efficient conjugation lengths and organized molecular stacking, which enhance charge transport and reduce degradation during cycling [25]. Additionally, R. Yue et al., copolymerized 1,12-bis(carbazolyl)dodecane (2Cz-D) and 3,4-ethylenedioxythiophene (EDOT) electrochemically, the copolymer exhibited a crosslinked structure instead of being a composite or a blend of the two homopolymers. The well-ordered molecular stacking of EDOT-Carbazole copolymers enhances their electrochemical properties by improving redox activity and electrochemical stability. This ordered structure facilitates efficient charge transport and reduces electrical resistance, leading to higher electrical conductivities than homopolymers [26].

Additionally, the insertion of Polyhedral Oligomeric Silsesquioxane (POSS) units into conductive polymers markedly affects their stability and optical absorbance. POSS units, characterized by their distinctive cubic architecture, function as scaffolds that can affect the organization and conjugation of polymer chains, prevent excessive π-π stacking, and suppress excimer formation, this affords to modulate the optical properties[27].

Numerous studies have investigated the incorporation of POSS units into polycarbazole-based materials to enhance their properties. Yu-fang et al. discovered that incorporating POSS units increased the stability and enhanced the dispersity of the polymers, inhibited interchain aggregation, improved optical properties by improving charge balancing, and increased brightness, current efficiency, and purer blue light emission [28]. Similarly, Imae et al. synthesized a novel polyhedral oligomeric silsesquioxane containing carbazole (POSS-Cz) via hydrosilylation in the presence of a platinum catalyst. It was determined that the

POSS core effectively isolated each carbazole through steric and electronic effects, providing a valuable concept for developing innovative photo- and electroactive materials [29].

Incorporating POSS units into poly(3,4-ethylenedioxythiophene) (PEDOT) offers several potential benefits, particularly in enhancing electrochemical stability and optiming its optical and morphological characteristics, making it suitable for advanced applications. The Cihaner group synthesized ethylene dioxythiophene containing pendant POSS units (PEDOT-POSS) in this context. The electrochemical study of the results showed that the addition of POSS units to the backbone of the polymers caused an increase in the electrochemical stability of the electroactive polymers without causing any significant changes in optical behaviors [30].

This work explores the dynamic multichromic characteristics of a copolymer synthesized electrochemically by copolymerizing EDOT and octakis(hydrodimethylsiloxy)octasilsesquioxane (octasilanePOSS) to form an OctaCarbazole.POSS-EDOT-based electrochromic copolymer. It studies the effect of incorporating POSS units into its structure, highlighting adjustable color-switching abilities and prospects for advanced optoelectronic applications.

II. Material And Method

3,4-ethylenedioxythiophene (EDOT), N-vinyl carbazole, platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Pt(dvs)), tetrabutylammonium hexafluoro phosphate (TBAPF6), Dichloromethane (DCM, anhydrous, 99.8%) degassed with nitrogen before use. all the solvents were obtained from Sigma Aldrich. The solvents were freshly distilled. Octasilane-POSS was purchased from Hybrid Plastics, while OctaCBZ-POSS was synthesized according to Imae's procedure (check app. for H-NMR result)[29]. Electrochemical polymerization studies and copolymer measurements were recorded using a Gamry PCI4/300 and Gamry Reference 600 potentiostat–galvanostat at room temperature. The ^{1}H-NMR spectra of the synthesized materials were obtained using a Bruker Spectrospin Avance DPX-400 spectrometer. The samples were dissolved in $CDCl_3$, with chemical shifts referenced to tetramethylsilane as the internal standard. Colorimetric measurements were recorded using a Specord S600 (equipped with a standard D65 illuminator and a 108° field of view). The International Commission on Illumination defined the color space based on luminance (L), hue (a), and intensity (b). The colorimetric standards used were platinum cobalt DIN ISO 621, iodine DIN EN 1557, and Gardner DIN ISO 6430.

Electrochemical measurements were performed with a Gamry PCI4/300 and Gamry Reference 600 potentiostat/galvanostat at room temperature. Spectroelectrochemical experiments were conducted with a Specord S600 Spectrometer. In situ, optoelectrochemical spectra of the films were acquired at different applied potentials. A square wave potential technique was employed, applying a constant potential between the neutral and oxidized states to assess the electrochemical stability and switching behavior of the polymer films. The electroactivity of the films was then compared to their initial values using cyclic voltammetry. The electrolyte solution for the electrochemical studies was prepared by dissolving tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in dichloromethane. A three-electrode setup was used, consisting of a glassy carbon (GC) working electrode (0.071 cm²), a platinum wire counter electrode, and an Ag/AgCl reference electrode. A solution containing EDOT, and OctaCBz-POSS, in 3 ml of 0.1 M $TBAPF_6$/DCM was prepared. Polymerization was conducted by cycling the potential from -1 V to +1.5 V for 15 cycles, with a scan rate of 100 mV s^{-1}. The resulting copolymer film on GC was rinsed with DCM to remove residual monomers and electrolytes. For the Optoelectrochemical study, the polymerization process was conducted electrochemically using constant potential electrolysis on an indium-tin-oxide (ITO) electrode (Delta. Tech. 8–12 X, 0.7x5.0 cm²). Switching times, and Coloration efficiency were measured at 570 nm using chronoamperometry with 10 s intervals using these equations:

Switching time $\Delta T\% = T_{final}\% - T_{initial}\%$

Coloration efficiency $CE = \frac{\Delta OD}{Q}$

where: $\Delta OD = \log (T_{bleached}/T_{colored})$, and Q: Charge density (charge per unit area, in C/cm²).

The measurements were conducted in situ utilizing a three-electrode configuration, comprising indium tin oxide (ITO) as the working electrode, a platinum wire as the counter electrode, and a silver wire as the reference electrode, all situated within a UV cuvette. all experiments were conducted at 25 °C.

III. Results And Discussion

Electrochemical properties of EDOT and Octa-CBz-POSS Monomers and their Copolymer.

The electrochemical behavior of the monomers was initially examined by cyclic voltammetry by using a three-electrode cell in a solution of 0.1 M $TBAPF_6$/DCM to obtain the appropriate copolymer. **Figure 1** shows Octa-CBzPOSS's irreversible oxidation peak at around 1.5 V vs Ag/AgCl. However, Octa-CBzPOSS film cannot be obtained due to the solubility problem of the formed film. Additionally, PEDOT exhibited an irreversible oxidation peak at 1.59 V relative to Ag/AgCl as shown in **Figure 1.** Based on that, it is possible to copolymerize monomers to obtain the copolymer through potentiodynamic electrolysis or constant potential. The cyclic voltammetry of the mixture containing both monomers was examined, and the chemical structures of EDOT, Octa-CBz-POSS, and their corresponding copolymer poly (EDOT-co-OctaCBz-POSS) are shown in **Scheme 3**. The repeating cyclic voltammogram of the EDOT and Octa-CBzPOSS monomers feed ratio (1:1) is given in **Figure 2**.

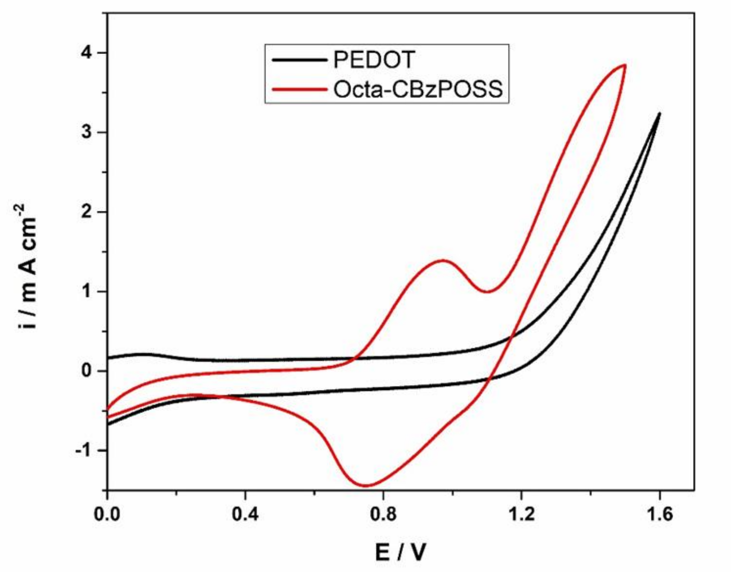
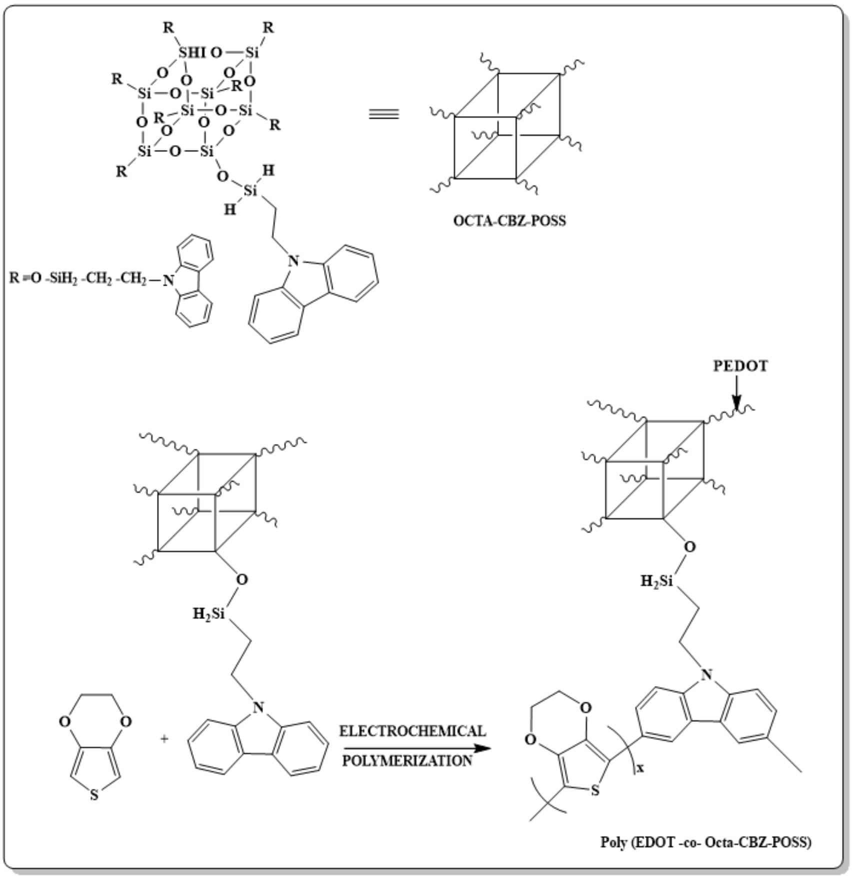


Figure. 1. Electrochemical behaviors of Octa-CBzPOSS and EDOT on a GC electrode in 0.1 M TBAPF$_6$/DCM with a scan rate of 100 mV s^{-1}.



Scheme 3. Chemical structures of EDOT, Octa-CBz-POSS, and their corresponding copolymer poly (EDOT-co-OctaCBz-POSS).

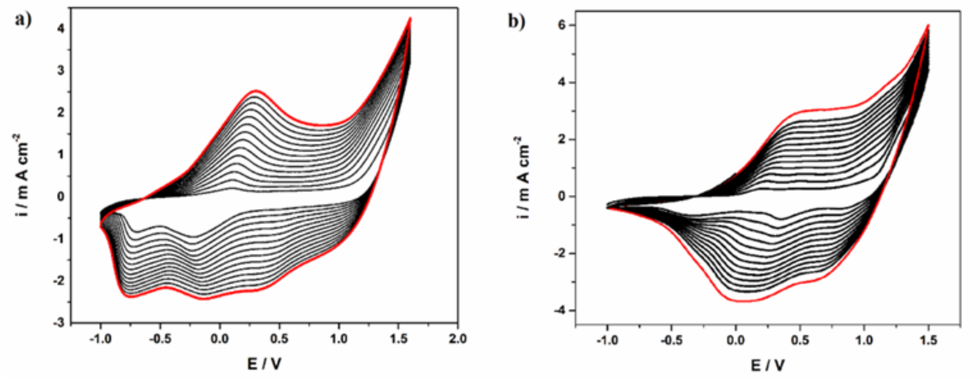


Figure 2. The repeating cyclic voltammogram of **a)** EDOT, and **b)** Octa-CBzPOSS and EDOT monomers on a GC electrode in 0.1 M $TBAPF_6$/DCM with a scan rate of 100 mV s^{-1}.

As illustrated in **Figure 2 b.**, the cyclic voltammogram obtained after a specified number of potentiodynamic scans between −1.0 V and 1.5 V exhibited an increase in the redox wave currents, indicating an increase in the polymer amount on the electrode surface and demonstrating the formation of a conjugated polymer film. The result was an insoluble polymer, poly (EDOT-co-OctaCBz-POSS) copolymer film, since upon successive scans, the polymer film displayed two reversible redox pairs indicative of the doping at 0.2 V and 1.5 V and de-doping processes at 0.35 V, increasing as a function of the number of scans.

To understand the effect of incorporating OctaCBz-POSS units into a PEDOT backbone, further investigations of the electrochemical properties of the PEDOT-co-OctaCBz-POSS copolymer were performed. Cyclic voltammetry was studied at various scan rates (20 to 200 mV/s) to evaluate the kinetics of charge transfer and film formation. The results showed well-defined anodic and cathodic peaks, demonstrating reversible redox processes and uniform copolymer deposition. Moreover, peak currents scaled linearly with the square root of the scan rate, suggesting a diffusion-controlled process as shown in **Figure 3**. This response indicates that the copolymer retains its electrochemical activity at high scan rates, which is crucial for applications necessitating quick switching, such as in electrochromic devices. The ability to maintain performance at varying scan rates reflects the stability of the copolymer structure, which is crucial for long-term stability in electrochemical applications.

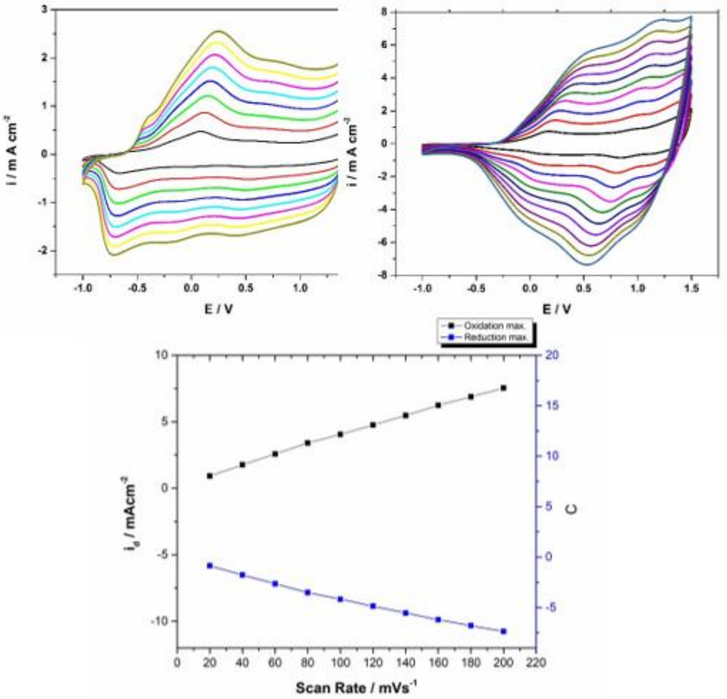


Figure 3. Scan rate experiments for: **a)** PEDOT, b**)** Poly (EDOT-co-OctaCBz-POSS) copolymer at various scan rates (a) 20, (b) 40, (c) 60, (d) 80, (e) 100, (f) 120, (g) 140, (h) 160, (i) 180, and (j) 200. **c)** The current vs. scan rate plot of the copolymer poly (EDOT-co-OctaCBz-POSS) film with increasing scan rate in 0.1 M $TBAPF_6$/DCM.

Electrochemical stability investigations were conducted using cyclic voltammetry (CV) to evaluate the enhancement effect of the OctaCBz-POSS unit within the PEDOT chain structure. As shown in Figure 4a, the PEDOT film gradually loses its electroactivity when switching the polymer film between its neutral and oxidized states multiple times at a scan rate of 100 mV/s; after 60 cycles, it loses approximately 80% of its electroactivity. While the copolymer retains about 25% of its electroactivity after 120 cycles, as illustrated in **Figure 4 b.** Compared to Poly (CBz-co-EDOT)[23], it was found that this polymer lost electroactivity after 60 cycles, which further proves the effect of the POSS unit in the copolymer. The stability of poly (EDOT-co-OctaCBz-POSS) is demonstrated by CV curves exhibiting minimal variations in redox potentials and a reduced decline in peak current over many cycles, signifying enhanced charge retention and reversibility. Furthermore, due to the insufficient adhesion of PEDOT to the electrode surface[31] , the highly stable POSS unit improves PEDOT's adhesion. At the same time, its covalent incorporation into the backbone forms a star-like shape, ensures uniform dispersion, prevents phase separation, increases the distance between chains, and creates efficient ion transport pathways.

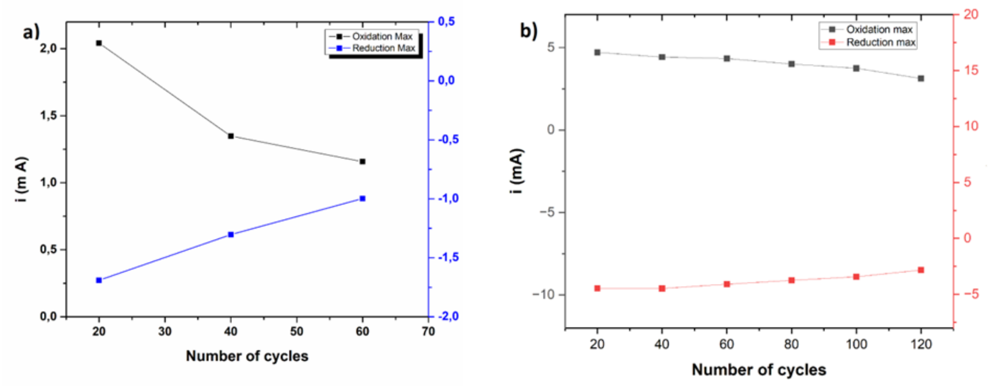


Figure 4. Stability tests for **(a)** PEDOT, and **(b)** poly (EDOT-co-OctaCBz-POSS) in 0.1 M TBAPF$_6$/DCM.

Spectro-electrochemical characterization of poly (EDOT-co-OctaCBz-POSS) copolymer.

The study of spectro-electrochemical characteristics of poly (EDOT-co-OctaCBz-POSS) copolymer is conducted by electrochemical deposition for the copolymer on an indium tin oxide (ITO) electrode using a constant potential at 1.6 V and compared to PEDOT, which is coated at 1.5 V. UV-Vis spectro-electrochemical analysis was performed over a potential range of -1 V to +1.5 V (vs. Ag/AgCl), then the electronic absorption spectra were recorded in a free monomer medium of 0.1 M TBAPF$_6$/DCM, with the findings presented in **Figure 5**. and **Table 1**.

Table 1. Optical properties PEDOT and poly (EDOT-co-OctaCBz-POSS) copolymer on ITO in 0.1 MTBAPF$_6$/DCM.

Polymers	λmax (nm)	Ega (eV)	t switching (s)	CE (C/cm2)
PEDOT*	600	1.6	1.2	352
Co-Polymer	570	1.8	1	245

* PEDOT values as reported by Cihaner et al. Adapted with permission from the ref [30]

UV-Vis spectroscopy reveals distinct differences in the optical characteristics of poly (EDOT-co-OctaCBz-POSS) compared to PEDOT. In its neutral state, the copolymer exhibits a broader absorption band (λ_{max} 570 nm) in the visible region, attributed to π-π* transitions, and displays a slight hypsochromic shift compared to PEDOT, which shows its π-π* transitions at 600 nm. During electrochemical oxidation, new bands between 700 and 850 nm in the near-infrared spectrum for the copolymer, indicating the generation of charge carriers: polaron and bipolaron. The optical band gap of the copolymer film was calculated from the absorption onset and found to be 1.8 eV; this value lies between the band gap values of PEDOT (1.6 eV) and polycarbazole.

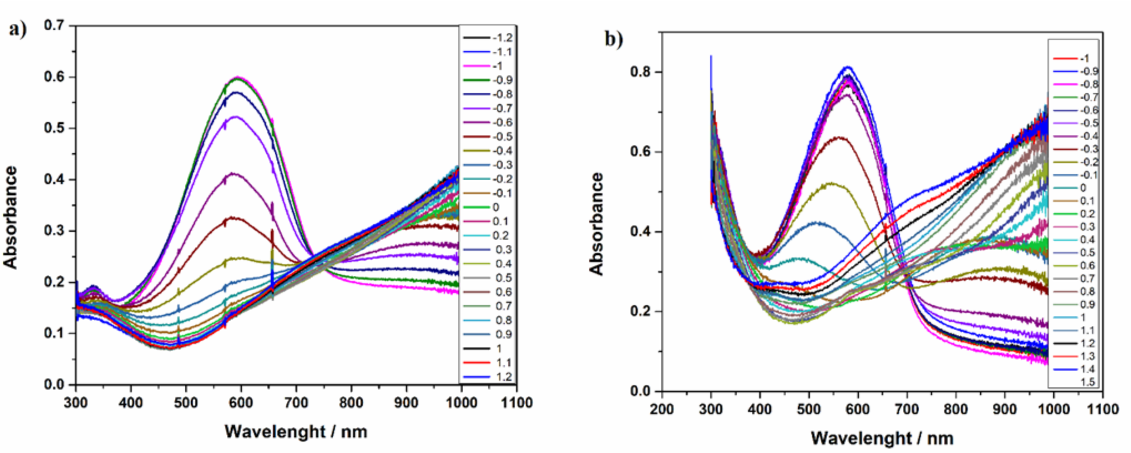


Figure 5. Electronic absorption spectra of **a)** PEDOT (25 mC/cm^2), and **b)** poly (EDOT-co-OctaCBz-POSS) (75 mC/cm^2) coated on ITO electrode at various applied potentials between-1.2 V and +1.5 V in 0.1 M TBAPF$_6$/DCM.

Although incorporating the OctaCBz-POSS unit into the PEDOT backbone increased the band gap—likely due to the star-like structure formed by OctaCBz-POSS that creates a network structure—the polymer has demonstrated excellent electrochromic properties; it exhibited multiple colors during oxidation and reduction processes. The electrochromic performance of the copolymer is assessed using Chronoabsorptometry, a spectroelectrochemical method that measures absorbance changes over time after applying a potential, to investigate the alterations in the material's color or light absorption induced by voltage. Chronoabsorptometry investigations clarify the copolymer's electrochromic performance by evaluating switching kinetics, optical contrast, and coloration efficiency. This is conducted using a potential (-1 V to +1.5 V vs. Ag/AgCl) on an ITO electrode in a 0.1 M TBAPF6/DCM free monomer solution. the results shown in **Table 1** and **Figure 6** revealed a rapid switching time compared to PEDOT (1.2 s-1) and Poly (CBz-co-EDOT), which was found to be 2.9 s-1. The copolymer based on OctaCBz-POSS and EDOT achieved higher coloration efficiencies and exhibited substantial changes in transmittance.

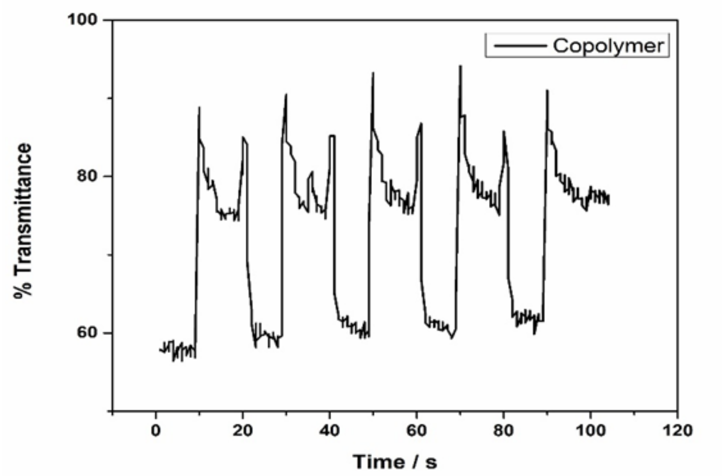


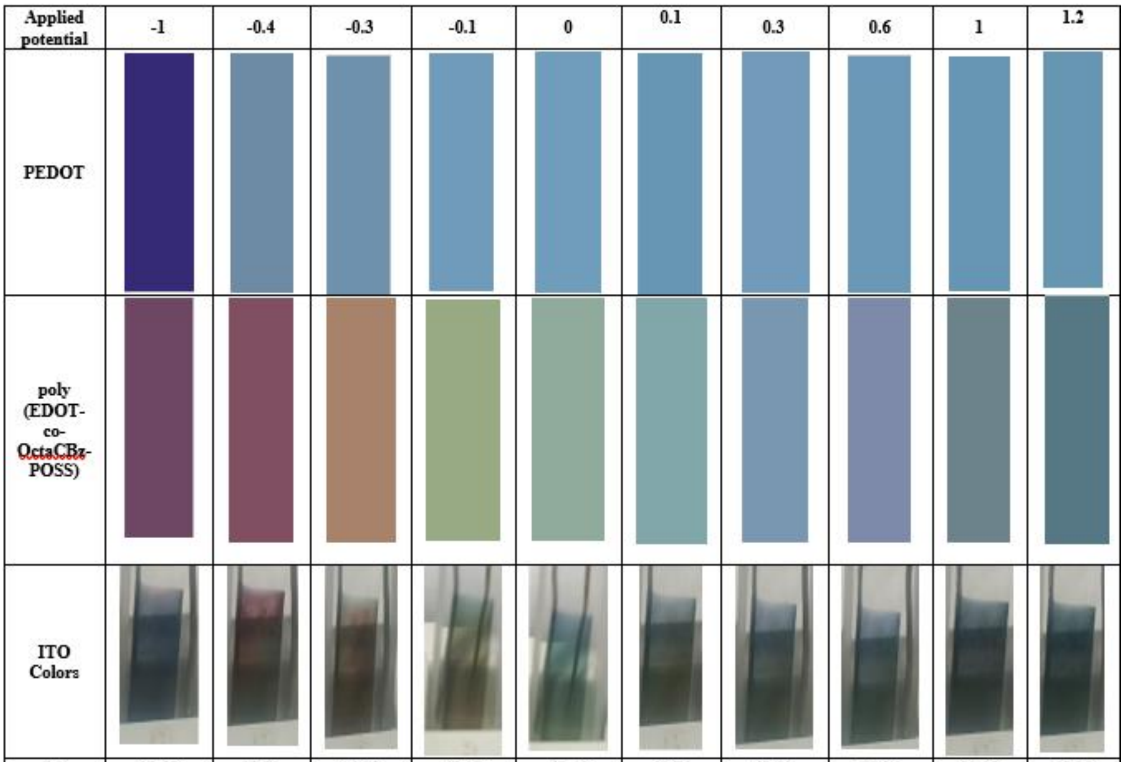
Figure 6. Chronoabsoptometry experiments for the copolymers when the polymer was switched for 10 s intervals between redox states in 0.1 M TBAPF$_6$/DCM on the ITO electrode.

The determined coloring efficiency, with values up to 245 cm²/C at 570 nm, signifies an effective modification of optical absorbance with low charge expenditure, surpassing that of Poly (CBz-co-EDOT) which has a CE value near 190cm²/C at 545 nm. This improved performance can be attributed to the polymer morphology resulting from the star-like shape formed by the OctaCBz-POSS unit, which facilitates rapid ion transport, reversible redox processes, and increased conductivity.

For quantitative evaluation of the copolymer's electrochromic performance, colorimetric analysis in the CIE Lab* color space was performed, highlighting its ability to produce reproducible color changes across redox states, which is essential for applications that require precise optical modulation. Colorimetry in the CIE

Lab* color space, established by the International Commission on Illumination (CIE), is extensively used to evaluate the electrochromic capabilities of conducting polymers. These polymers are valued for their adjustable optical properties in applications such as smart windows. The CIE Lab* system quantifies color through L* (lightness), a* (red-green axis), and b* (yellow-blue axis).

The colorimetric study of poly (EDOT-co-OctaCBz-POSS) demonstrated an extended spectrum of colors when the potential switched between -1 V and 1.5 V compared to PEDOT. Upon applying a potential, the copolymer traveled from a wide range of colors, from deep purple at -1.0 V to Crown at -0.3 V. Then color traveled from Greenstone at -0.1V to Cranberry blue at 0.3 V, and to blue-gray at 1.5 V, depending on the applied voltage. Meanwhile, PEDOT changed its color from light blue to deep blue when it transitioned from an oxidized to a neutral state. The finding is summarized in **Table 2**.



Applied potential	**-1**	**-0.4**	**-0.3**	**-0.1**	**0**	**0.1**	**0.3**	**0.6**	**1**	**1.2**
PEDOT										
poly (EDOT-co-OctaCBz-POSS)										
ITO Colors										
L*	35.57	39.82	46.25	65.15	67.45	65.76	60.81	57.36	53.08	48.23
a*	20.40	22.91	22.11	-1.12	-12.09	-12.48	-5.40	0.28	-7.05	-9.89
b*	- 9.60	-1.95	6.35	17.40	4.83	-5.88	-17.56	-18.08	-7.42	-11.4

Table 2. Colorimetry and optical comparisons of poly PEDOT, and Copolymer.

The copolymer demonstrated dynamic electrochromic properties by mapping the chromaticity coordinates (CIE 1931) derived from electronic absorption spectra at different applied potentials as shown in the **Figure 7**. It exhibited a wide range of color transitions across various redox states, representing a notable improvement over pristine PEDOT. This multichromatic property is attributed to OctaCBz-POSS, which induced morphological changes that led to the loosening packing of the polymer chains, allowing relatively free ion movement during the redox switching and inducing more distinct color changes. This highlights the potential for optimizing electrochromic properties by structural modifications.

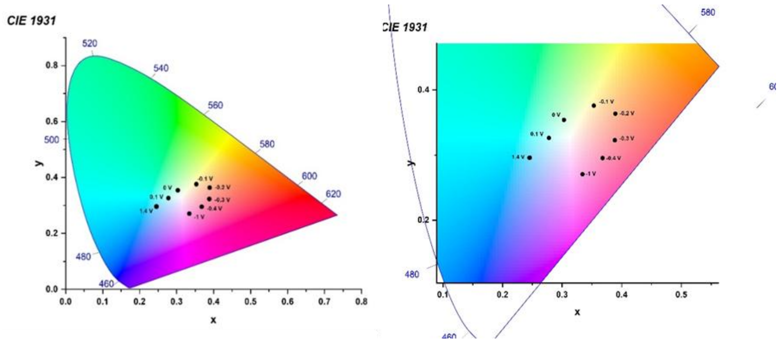


Figure 7. CIE 1931 color coordinates of poly (EDOT-co-OctaCBz-POSS) at different potentials.

IV. Conclusion

Incorporating OctaCBz-POSS units into the PEDOT backbone enhances the copolymer's electrochemical stability, which is essential for maintaining performance during prolonged use. Furthermore, it improves electrochromic and colorimetric adaptability, facilitating advancements in color-tunable technologies. Additionally, the significant contrast between the neutral and oxidized states, consistent cycling performance, and the polymer's low oxidation potential enable efficient electrochromic switching, which is critical for applications in smart windows and displays. Overall, the combination of these properties highlights the polymer's versatility and significantly underscores its potential to advance the field of electrochromic materials.

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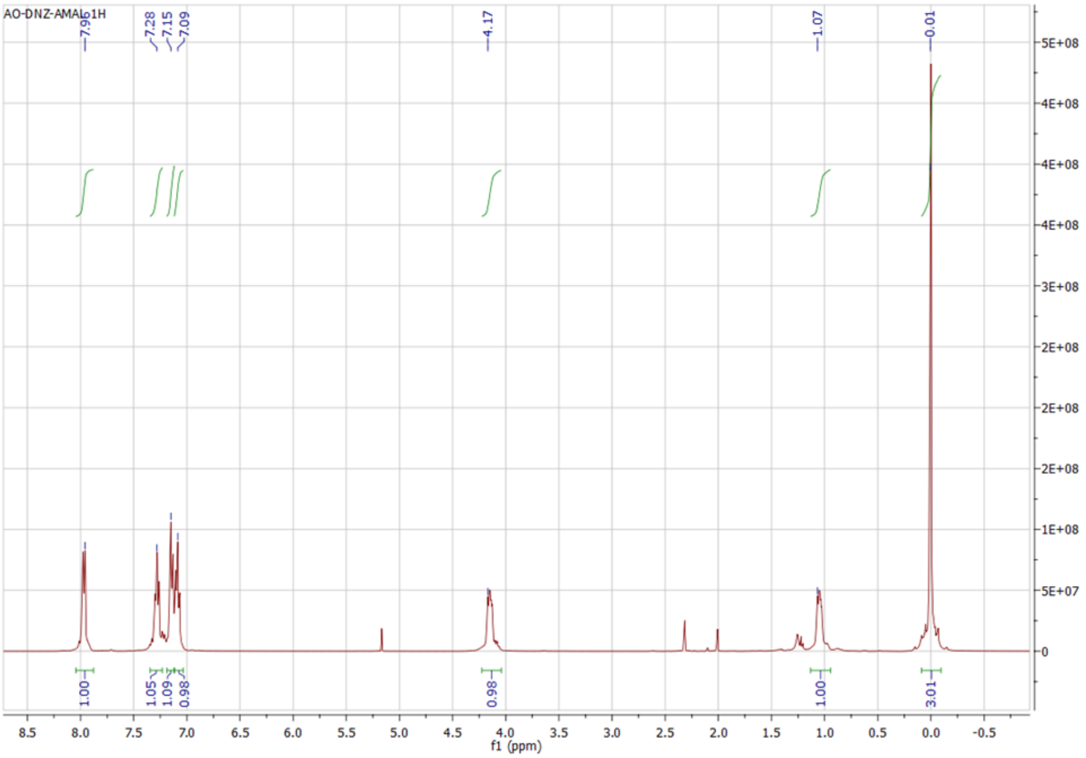
Appendix



H-NMR spectra of OctaCBz-POSS molecule.