

## A Low Band Gap Benzimidazole Derivative and Its Copolymer with 3,4-Ethylenedioxythiophene for Electrochemical Studies

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A novel monomer; 2-(3-nitrophenyl)-4,7-di(thiophen-2-yl)-1H-benzo[d]imidazole) (BIMN) was used for electrochemical copolymerization with 3,4-ethylenedioxythiophene (EDOT). Polymerization was achieved in acetonitrile (ACN)/dichloromethane (DCM) (1:1, 1:3 and 1:5, molar ratios) solution containing sodium perchlorate (NaClO<sub>4</sub>) and lithium perchlorate (LiClO<sub>4</sub>) mixture as the supporting electrolyte on an ITO electrode. The chemical structures of monomer and copolymers were characterized by nuclear magnetic resonance (<sup>1</sup>H NMR) and scanning electron microscopy (SEM). The optical and electrochromic properties were investigated by UV-vis spectrophotometer and cyclic voltammetry, respectively. Combination of BIMN and EDOT provides lower oxidation potential, lower bandgap and higher optical contrast.

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Great efforts have been focused on the design and synthesis of conducting polymers to achieve desirable properties for applications such as organic solar cells, biosensors<sup>1,2</sup> and electrochromic devices.<sup>3–5</sup> Over the last two decades conducting polymers (CPs) have received considerable attention due to their electrochemical and optical properties,<sup>6–8</sup> low cost, tunable band gaps<sup>3–5</sup> and fast switching times.<sup>9</sup> Modification of bandgap of conducting polymer is a crucial strategy to achieve desirable electrochromic properties. In order to design a low bandgap material, donor–acceptor approach is one of the most plausible ways. In accordance with this approach, regular alternation of donor unit with a high HOMO level and an acceptor unit with a low LUMO level along a conjugated chain is proposed. Moreover, combination of donor and acceptor moieties in the polymer backbone not only enhances D-A interactions but also helps to improve optical, mechanical and electronic properties.<sup>10</sup>

Recently, different kind of molecules like benzothiadiazole (BTd), quinoxaline and benzotriazole (BTz) are widely used as the electron deficient units. Especially, benzimidazole (BIm) has some attractive properties since the presence of both imine and amine nitrogen in its structure provides desired bandgap and optical properties. These DAD type conjugated molecules can be synthesized either by chemical or electrochemical polymerizations.<sup>11,12</sup> Electrochemically generated copolymerization offers efficient modification of the structures of conjugated polymers, enable control the bandgap of conducting polymer.<sup>13</sup> Homogeneous copolymerization can be achieved at the electrode surface through which the film thickness is controlled. Copolymerization is a very promising and efficient method to improve electrochemical properties of the conducting polymers.<sup>3-5</sup> In addition to these promising properties BIm unit has some drawbacks such as low stability and poor electrochromic contrasts.<sup>11,12</sup> To overcome these, copolymerization is an easy and effortless method to combine electrochromic properties of the comonomers and acquiring low oxidation potentials.<sup>14</sup> 3,4- Ethylenedioxythiophene (EDOT) is a good candidate as a co-monomer since it leads to a low bandgap polymer than thiophene due to the presence of two electron donating oxygen atoms. Moreover, it contributes to fast switching times, high conductivity and good stability in ambient conditions.<sup>15</sup>

Furthermore, copolymerization is a facile method to combine and enhance optical and kinetic properties.<sup>11,12</sup> Low oxidation potential and high stability of EDOT makes it a possible candidate for copolymerizations to enhance the electrochemical properties of resulting copolymers. Electrochemical properties of copolymers of EDOT have

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been also widely studied previously.<sup>16–18</sup> However, to the best of our knowledge, use of a novel BIMN for that matter has not yet been reported.

In this work, 2-(3-nitrophenyl)-4,7-di(thiophen-2-yl)-1Hbenzo[d]imidazole) (BIMN) (Scheme 1) was synthesized. The structure of conducting polymer was analyzed by spectral methods (<sup>1</sup>H, <sup>13</sup>C NMR) and the morphology was characterized using scanning electron microscopy (SEM). In addition, electrochemical copolymerization was undertaken by cyclic voltammetry with a mixture of BIMN and EDOT monomers in acetonitrile (ACN)/dichloromethane (DCM) solution. Electrocopolymerization was achieved in different ratios of comonomers such as 1:1, 1:0, 1:3 and 1:5 BIMN:EDOT. The copolymers were characterized by UV-visible absorption spectroscopy (UV-Vis), scanning electron microscope (SEM), spectroelectrochemistry and kinetic studies.

## Experimental

*Materials.*— Bromine, 2,1,3-benzothiadiazole, ammonium cerium (IV) nitrate, ethyl acetate, chloroform, dichloromethane, bis(triphenylphosphine)palladium (II) dichloride, 3-nitrobenzaldehyde, thiophene, n-butyllithium solution (2.5 M in hexane), tributyltinchloride sodium perchlorate (NaClO<sub>4</sub>) and



Scheme 1. Synthetic route of monomer synthesis. *i*: Br<sub>2</sub>/HBr, *ii*: NaBH<sub>4</sub>/ethanol, *iii*: (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub>/H<sub>2</sub>O<sub>2</sub>/acetonitrile, *iv*: Pd(Ph<sub>3</sub>)<sub>2</sub>Cl, dry THF.



Scheme 2. Schematic illustration of the copolymerization.

lithium perchlorate (LiClO<sub>4</sub>) were purchased from Sigma-Aldrich. Hydrobromic acid was purchased from Acros. Tetrahydrofuran was purchased from Fisher and purified over benzophenone and sodium.

*Equipment.*— Electropolymerization was performed with a Gamry instruments Reference 600 potentiostat/galvanostat/ZRA in a threeelectrode cell consisting of indium tin oxide (ITO) coated glass slide as the working electrode. A platinum wire as the counter electrode, and a Ag wire as the pseudo reference electrode were employed. For the spectroelectrochemical studies of the polymer films Varian Cary 5000 UV-Vis spectrophotometer was used in order to determine the absorption bands of both neutral and oxidized states of the polymers. For surface imaging of the electrodes, scanning electron microscope (SEM) (JEOL JSM-6400 model) was used. To confirm the structures of the monomers, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> on Bruker Spectrospin Avance DPX-400 spectrometer and the chemical shifts were expressed in ppm relative CDCl<sub>3</sub> as the internal standard. HRMS data were recorded on Waters SYNAPT MS System to confirm the monomer synthesis.

Synthesis of the monomer (BIMN).—Synthesis of 4,7-dibromo-2(3-nitrophenyl)-1H-benzo[d]imidazole (4).— Synthesis of the acceptor group was achieved in accordance with the literature.<sup>19,20</sup> Firstly, 3,6-dibromobenzene-1,2-diamine (3) was synthesized as a result of bromination and further reduction of 2,1,3-benzothiadiazole (1) in ethanol was carried out by NaBH<sub>4</sub>. Then, compound 3(1.50 g, 5.6 mmol) was dissolved in acetonitrile (ACN) (9.0 mL) at room temperature. After dropwise addition of H<sub>2</sub>O<sub>2</sub> (0.54 mL, 23 mmol) and 3-nitrobenzaldehyde (0.85 g, 5.6 mmol), ammonium cerium (IV) nitrate (0.3 g, 0.6 mmol) was added to the solution. The reaction was left to stirring overnight and ended with TLC monitoring. Subsequently, the reaction mixture was poured into the ice/water bath and filtered for the solids. The residue was washed with the ACN and the acceptor group (4) was yielded as light pink solid (0.40 g, 1.08 mmol, 20%).<sup>21</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  12.78 (s, 1H), 8.84 (s, 1H), 8.50 (d, 1H, *j* = 7.82 Hz), 8.30 (d, 1H, *j* = 8.21 Hz), 7.67 (t, 1H, *j* = 8.01 Hz), 7.31 (s, 2H).<sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$ 158.5, 148.4, 143.6, 134.7, 133.9, 131.9, 127.3, 124.2, 121.3, 104.8.

Synthesis 2-(3-nitrophenyl)-4,7-di(thiophen-2-yl)1Hof benzo[d]imidazole (BIMN).-To synthesize the corresponding 4,7-dibromo-2(3-nitrophenyl)-1H-benzo[d]imidazole monomer, (4) (0.40 g, 1.08 mmol) was dissolved in dry THF. Subsequently, tributyl(thiophene-2-yl)stannane (1.99 g, 5.40 mmol)<sup>22</sup> was added to stirred solution under argon atmosphere. The mixture was heated at reflux temperature for 45 minutes. Afterwards bis(triphenylphosphine)palladium (II) dichloride was added as the catalyst and the reaction proceeded in reflux under argon atmosphere for 16 hours with TLC monitoring. The solvent was evaporated and product (BIMN) was purified by column chromatography as pale yellow solid (eluent: Chloroform:Hexane, 3:1) (0.74 g, 0.18 mmol, 17%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  11.96 (s, 1H), 8.34 (d, 2H, *j* = 8.29 Hz), 8.08-8.04 (m, 3H), 7.89 (s, 1H), 7.66–7.45 (m, 4H), 7.23 (d, 2H, *j* = 7.0 Hz).<sup>13</sup>C NMR(CDCl<sub>3</sub>):  $\delta$ 152.2, 149.8, 141.4, 137.8,

133.7, 132.0, 130.6, 128.6, 127.1, 126.5, 125.3, 123.8, 123.0, 121.8. HRMS: Calculated  $[M]^+ = 404.0527$ , Measured  $[M]^+ = 404.0515$ . preparation of BIMN and copolymer film by The electropolymerization.-Electrochemical polymerization of BIMN was performed on indium tin oxide (ITO)-coated glass slides using equimolar 0.1 M sodium perchlorate (NaClO<sub>4</sub>) and lithium perchlorate (LiClO<sub>4</sub>) as the supporting electrolyte in a mixture of dichloromethane (DCM) and ACN (5:95, v/v) with repeated scan intervals between 0 and 1.40 V versus Ag wire pseudo reference electrode. Polymerization of EDOT was also achieved on ITO-coated glass slides using 0.1 M sodium perchlorate (NaClO<sub>4</sub>) and lithium perchlorate (LiClO<sub>4</sub>) containing 5:95 (DCM : ACN) solution with repeated scan intervals between -1.0 and 1.5 V. It was seen that PBIMN forms an orange polymer film on the electrode surface.

Electropolymerizations (BIMN:EDOT) were performed in 1:1 (0.86: 0.86 mM); 1:3 (0.86: 2.58 mM) and 1:5 (0.86: 4.3 mM) concentration ratios of BIMN and EDOT using 0.1 M NaClO<sub>4</sub>, LiClO<sub>4</sub> supporting electrolyte in 3.0 mL 5:95 (v/v) DCM:ACN solution with repeated scan intervals between -1.0 and 1.5 V versus Ag wire pseudo-reference electrode (Figure 2). Schematic illustration of the copolymerization was illustrated in Scheme 2. The use of perchlorates enhances good polymer film formation on the electrode surface. The size difference between the anion and the cation of the supporting electrolyte facilitates doping-dedoping processes.

## **Results and Discussion**

*Electrochemical properties of PBIMN and copolymers.*— Electrochemical and spectral studies were conducted as further characterization techniques to get a deeper knowledge on the properties of both homopolymers and copolymers. BIMN is a novel monomer and its electrochemical properties were not discussed before, hence in each section these results will be discussed together with (BIMN: EDOT) copolymers. For electrochemical polymerization and copolymerizations 10 cycles of CV were run to make a comparison with those of related polymers.

After the electrochemical synthesis of both BIMN and (BIMN: EDOT) copolymers, electroactivity of the polymers and the oxidation–reduction potentials were also determined via cyclic voltammetry technique. The cyclic voltammogram (CV) was performed on indium tin oxide (ITO) coated glass slides with 0.1 M (DCM : ACN) (5/95, v/v) solution in the presence of NaClO<sub>4</sub> and LiClO<sub>4</sub> as the supporting electrolytes. In Figure 1a, after formation of the irreversible monomer oxidation in the first cycle, a new reversible redox couple with an increasing current intensity appeared which proves the formation of electroactive polymer film of BIMN (PBIMN). Then to investigate the p-type and n-type doping properties of the polymer, CV was recorded in a monomer free solution (0.1 M LiClO<sub>4</sub>/ACN).

PBIMN has only p-type doping character with a reversible redox couple at 1.12 V. HOMO energy level was calculated from the onset potential of oxidation peak as -5.63 eV for PBIMN. The results were calibrated with respect to Fc/Fc<sup>+</sup> and the band energies were calculated relative to the vacuum level considering that the value of SHE is -4.75 eV vs vacuum. Figure 1 shows the CV of BIMN (a)



Figure 1. a) Repeated potential scan polymerization of **BIMN** in 0.1 M LiClO<sub>4</sub>/NaClO<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>/ACN (5:95, v:v) solution b) Single scan cyclic voltammogram of **PBIMN** in a monomer free 0.1 M LiClO<sub>4</sub>/NaClO<sub>4</sub>ACN solution on an ITO electrode.

and PBIMN (b) which were run between 0 V and 1.4 V at a scan rate of 100 mV/s.

Colors and electrochemical properties of the CPs can be controlled via copolymerization technique. It is not only a simple strategy but also has significant effects on the properties of these materials such as oxidation potential, HOMO energy levels,  $E_g$  and  $\lambda_{max}$ values. In literature, this strategy was applied for different CPs to improve the mentioned properties.<sup>3–8</sup> Due to outstanding electrochemical properties such as; low oxidation potential, good stability and low bandgap, EDOT is one of the excellent candidates for electrochemical copolymerization.<sup>23</sup>

As a result, in this study copolymerization technique was applied to improve the electrochemical properties of this novel monomer (BIMN) by insertion of EDOT unit. Three novel BIMN and EDOT based copolymers with (1:1), (1:3) and (1:5) (BIMN: EDOT) ratios were synthesized electrochemically to observe the effect of increasing EDOT ratio on the mentioned properties of resulting copolymers.

Figure 2 illustrates the cyclic voltammogram for electrochemical polymerization of BIMN(d), EDOT (e) and 1:1 (a) 1:3 (b) 1:5 (c) (BIMN:EDOT) copolymers to observe the effect of EDOT unit with different ratios to the polymer backbone. In addition, to investigate the oxidation potentials and HOMO energy levels, single scan cyclic voltammograms for three different copolymers were recorded in 0.1 M LiClO<sub>4</sub>/NaClO<sub>4</sub>- ACN solution on an ITO electrode and reported in Figure 3. Both Figure 3 and Table I show that 1:1 (a) 1:3 (b) 1:5 (c) (BIMN:EDOT) copolymer films revealed reversible redox couple at positive potentials pointed at 0.44 V, 0.45 V and 0.51 V versus Ag wire pseudo-reference electrode, respectively.

It is generally known that EDOT bearing D-A-D type polymers/copolymers have lower oxidation potentials compared to thiophene bearing ones due to the electron rich character of this group which makes easy to undergo any redox process. In the light of this knowledge, the significant decrease on the oxidation potential of (BIMN:EDOT) copolymers with respect to pristine PBIMN could be explained by the electron rich character of EDOT (Figure 2).

In this study, similar to the PBIMN, all BIMN and EDOT bearing copolymers are p-type dopable as illustrated in Figure 3. HOMO energy levels were calculated from the onset potential of oxidation peaks as -4.44 eV, -4.58 eV and -4.63 eV for (BIMN:EDOT) copolymers, respectively.

In order to designate the scan rate dependence of doping- dedoping processes, single scan cyclic voltammograms of (BIMN:EDOT) copolymers were recorded at different scan rates (50, 100, 150, 200 mV/s). This experiment could be used to prove whether these processes (doping-dedoping) are diffusion controlled or not. As seen in Figure 4, linear relationship between the current density and the scan rate was observed which shows that the electroactive polymer films were well adhered on the ITO surface and the redox processes were non-diffusion controlled for all copolymers ((a,b) 1:1, (c,d) 1:3, (e,f) 1:5 (BIMN:EDOT) copolymers.<sup>24</sup>

Table I represents electrochemical, spectroscopic and electrooptical parameters measured for these polymers.

These references from the literature were chosen according to general structure of acceptor unit namely benzimidazole unit. As seen in Scheme 3 all polymers are benzimidazole derivatives (Scheme 3).

These molecules have the same acceptor unit which affects electrochemical and optical properties of the polymers. Also all these derivatives were polymerized electrochemically and for each polymer 10 cycle polymerization was performed. This similar conditions of preparation make easy and reliable comparison of PBIMN with these molecules. Electrochemical polymerization potential ranges were also reported as 0.5 V/ 1.8 V for PBIBA, -0.3 V/ 1.5 Vfor PBIED and -0.5 V/ 1.8 V for PTTBI.

Benzimidazole based studies in literature were discussed in Tables I and II. Electrochemical, spectroelectrochemical and kinetic properties of both PBIMN and EDOT bearing copolymers were compared with three different donor-acceptor-donor type conjugated polymers. In the literature EDOT bearing D-A-D type polymers/copolymers generally have lower oxidation potentials compared to other derivatives because of the electron rich character of EDOT unit. The significant decrease in the oxidation potential of (BIMN:EDOT) copolymers with respect to PBIMN is clearly shown in Table I. In addition, when both PBIMN and copolymers are compared with those from literature (Refs. 26-28) both have very low oxidation potentials compared to other benzimidazole derivatives. Moreover, similar trend was observed for  $\lambda_{max}$  and  $E_g^{op}$  values. Insertion of EDOT into the polymer backbone causes red shift with higher  $\lambda_{max}$  and lower  $E_g^{op}$  values. Tailoring bandgap is important for donor-acceptor-donor type molecules since one can change and enlarge the area of application for these materials via this technique.

Spectroelectrochemical Studies of PBIMN and copolymers.— Electro-optical properties of the polymer films are important to determine the proper application fields of these materials and also to improve these structures via modifications. The changes in electronic absorption spectra upon doping/dedoping processes lead to investigate the optical and structural responses of the polymer films. Spectroelectrochemical changes of electrochemically synthesized polymers and copolymers were observed by monitoring in situ UV–Vis–NIR spectra in a 0.1 M NaClO<sub>4</sub>–LiClO<sub>4</sub>/ACN monomer free medium.



Figure 2. Cyclic voltammogram of 1:1 (a) 1:3 (b) 1:5 (c) (BIMN:EDOT) copolymers, BIMN(d) and EDOT (e).

Polymer/copolymer films were reduced to their neutral states by applying constant potential before oxidation. After removal of any trapped charge and dopant ion, the neutral film absorption and the changes in the absorption spectra upon stepwise oxidation were recorded by using UV–Vis–NIR spectrophotometer.

Spectroelectrochemistry studies combine electrochemical and spectroscopic techniques that can be operated at the same time. Hence it can provide information on both electrochemical and optical characteristics of all states of the polymers. In addition via this technique, one can get and calculate some important parameters for conducting polymers such as;  $\lambda_{max}$  values, optical bandgap ( $E_g^{op}$ ) and polaron/bipolaron bands.  $\lambda_{max}$  can be defined as the wavelength at which light is strongly absorbed by the absorbing species. This also gives crucial information on the colors of the polymers. From onset of the  $\lambda_{max}$ ,  $E_g^{op}$  could be calculated which can be defined as an energy difference (eV) between the valence band and the conduction band.

Figure 5 illustrates the  $\lambda_{max}$  values for the lowest energy  $\pi - \pi *$  transitions for PBIMN centered at 474 nm. In addition optical bandgap of the corresponding polymer was also calculated from the neutral state absorption onset as 1.97 eV.

PBIMN revealed multichromic behavior with an orange color in its neutral state ( $\lambda_{max} = 474$  nm) and blue color during stepwise oxidation, while intensity of absorption bands in the visible region decrease, new absorption bands (polaron and bipolaron bands) appear steadily in the NIR region (Figure 5). Then, fully oxidized state results in blue colored polymer. Spectroelectrochemical properties of 1:1(BIMN:EDOT), 1:3(BIMN:EDOT) and 1:5 (BIMN:EDOT) copolymers were also performed similar to those of homopolymer and results were summarized in Figure 6.

When electro-optical properties of homopolymer and copolymers were compared, insertion of electron rich EDOT unit into polymer backbone results in a significant red shift on the neutral state



Figure 3. Single scan cyclic voltammogram for 1:1 (a) 1:3 (b) 1:5 (c) (BIMN:EDOT) copolymers in 0.1 M LiClO<sub>4</sub>/NaClO<sub>4</sub> ACN monomer free solution on an ITO electrode (d) Single scan cyclic voltammograms for all (BIMN:EDOT) copolymers at different feed ratios.

Table I. Electrochemical ( $E_{ox}$  (V), HOMO (eV), LUMO (eV)) and optical properties ( $\lambda$ max (nm), Egop (eV)) of PBIMN, 1:1 (BIMN:EDOT) copolymer, 1:3 (BIMN:EDOT) copolymer and 1:5 (BIMN:EDOT) copolymer with respect to earlier studies.

	E <sub>ox</sub> (V)	HOMO* (eV)	LUMO (eV)**	$\lambda_{\max}$ (nm)	Eg <sup>op*</sup> (eV)
PBIMN	1.12	-5.63	-3.66	474	1.97
1:1	0.44	-4.44	-3.3	592	1.14
(BIMN:EDOT) copolymer					
1:3	0.45	-4.58	-3.46	605	1.12
(BIMN:EDOT)					
copolymer					
1:5	0.51	-4.63	-3.58	555	1.05
(BIMN:EDOT)					
copolymer					
Ref <sup>26</sup>	1.57	-6.1	-4.18	347/478	1.92
(PBIBA)					
Ref <sup>27</sup>	1.26	-5.31	-4.16	430/ 837	1.15
(PBIED)					
Ref <sup>28</sup>	1.43	-5.73	-4.13	_	1.60
(PTTRI)					

\*calculated with respect to reference <sup>25</sup>. ( $E_{ox}$  were calculated from Fig. 1 and Fig. 3;  $\lambda_{max}$  and  $E_g^{op}$  were calculated from Fig. 5 and Fig. 6). \*\*LUMO energy levels were calculated using HOMO energy levels and optical bandgap values.



Figure 4. Scan rate dependence of (a,b) 1:1 (c,d) 1:3 (e,f) 1:5 (BIMN:EDOT) copolymers in a 0.1 M NaClO<sub>4</sub>-LiClO<sub>4</sub>/ACN solution on an ITO electrode.

absorptions and 117 nm, 130 nm, 80 nm  $\lambda_{max}$  shifts with respect to PBIMN. As can be seen in Figure 6 absorption range in the visible region for copolymers were also enlarged with respect to that of PBIMN (Figures 5 and 6) and  $\lambda$ max values for 1:1, 1:3, 1:5 (BIMN:EDOT) copolymers were reported as 592 nm, 605 nm and 555 nm (Table I).

Optical band gaps for the three different copolymers were also calculated from the neutral state absorption onsets similar to the homopolymer and reported as 1.14 eV, 1.12 eV and 1.05 eV, respectively (Table I). Finally this tremendous decrease in the band gaps of copolymers compare to PBIMN could be due to the electron rich character of EDOT unit.

*Electrochromic contrast and switching studies of PBIMN and copolymers.*— Kinetic studies can be used to test the electrochemical stability of these types of polymers which is very crucial for the electrochromic device applications. In addition, electrochromic contrast and switching times can be monitored by potential stepping between two extreme states (neutral and oxidized) in a monomer-free solution The wavelengths at which kinetic studies recorded were determined from maximum absorbance values obtained in the spectroelectrochemical studies.

During kinetic studies, potential was set at an initial potential for a period of time, and was stepped to a second potential for the same period of time. Potentials were determined from single scan CV

![](_page_6_Figure_2.jpeg)

Scheme 3. Structures of the polymers chosen from the literature for comparison.

and each potential was applied for 5 s. From Fig. 7 optical contrasts and switching times were calculated. Optical contrast is the percent transmittance change at a given wavelength. The switching time is defined as the time required for one full switch between the two extreme states.

In this study, the stabilities, percent transmittance and switching times of the polymer films between their neutral and oxidized states were monitored in the near NIR region at 1190 nm for PBIMN and 1370 nm for 1:1 (BIMN:EDOT) copolymer in 0.1M LiClO<sub>4</sub>-NaClO<sub>4</sub>/ACN electrolyte/solvent couple.

PBIMN showed 22% transmittance change with a switching time of 0.3 s at 1190 nm. After copolymerization of BIMN and EDOT with 1:1 ratio, resulting copolymer displayed 53% transmittance change and 1.4 s switching time at 1370 nm (Figures 7 and 8). The 31% increase in the percent transmittance results may lead to possible application areas for such electrochromic materials.

This results illustrate that insertion of EDOT unit into the polymer backbone via copolymerization technique affects the kinetic parameters significantly. As summarized in Table II, I:1 (BIMN:EDOT)

Table II. Summary of kinetic and optic studies of PBIMN and 1:1 (BIMN:EDOT) copolymer.

	Wavelength (nm)	T%	Switching Times(s)
PBIMN	1190	22	0.3
1:1 (BIMN:EDOT) copolymer	1370	53	1.4
Ref <sup>26</sup> (PBIBA)	710	29	0.6
Ref <sup>27</sup> (PBIED)	1820	46	3.0
Ref <sup>28</sup> (PTTBI)	555	0.3	-

copolymer has better kinetic parameters then those of PBIMN in terms of optical contrasts in NIR region.

In the light of the points mentioned in results and discussion part, it can be clearly pointed out that insertion of EDOT yields (BIMN:EDOT) copolymers with lower oxidation potential, lower bandgap and higher optical contrast. These improved properties make the copolymers desirable for electrochromic applications.

Finally, effect of EDOT unit on the kinetic properties were investigated and compared with other benzimidazole derivatives in Table II. I:1 (BIMN:EDOT) copolymer showed the highest optical contrast as 53%. Compared to PBIED which contains EDOT as the donor unit, insertion of EDOT into copolymer backbone yields an increase of 7% in optical contrast.

Characterization.—Scanning electron microscopy (SEM) studies.- The morphologies of polymer films were investigated by scanning electron microscopy (SEM). All the figures were taken after 10 cycles of electrocopolymerization on ITO surface. Figure 9 shows the SEM images of the conducting polymer coated ITO electrode surfaces PBIMN, poly EDOT (PEDOT) and (BIMN:EDOT) copolymer. For the pure polymer, Figure 9A depicts the porous and cauliflower structure of a typical conducting polymer.<sup>21</sup> In Figure 9B, it can be observed that, the PEDOT film reveal a morphology composed of uniform surface. Also, it was clearly shown that polymer was spread over the electrode surface homogeneously. The surface of the (BIMN:EDOT) copolymer film changed drastically after the combination of the PBIMN or PEDOT and shows a porosity and a network. This change can be due to compatibility of the polymers. Compared with the PBIMN and PEDOT, the network surface of (BIMN:EDOT) copolymer film can be seen in Figure 9C-9D, which can be attributed to the effect of copolymerization. The results clearly indicate that copolymerization can lead to a different surface morphology, which may have an effect on the electrochromic performance.

![](_page_6_Figure_14.jpeg)

Figure 5. Electronic absorption spectra for (a) PBIMN film in 0.1 M NaClO<sub>4</sub>-LiClO<sub>4</sub>/ACN solution between 0.0 V and 1.15 V. (b) Colors of PBIMN at the neutral and oxidized states.

![](_page_7_Figure_1.jpeg)

Figure 6. Electrochemical p-type doping electronic absorption spectra of 1:1 (a) 1:3 (b) 1:5 (c) (BIMN:EDOT) copolymers in 0.1 M LiClO<sub>4</sub>/NaClO<sub>4</sub>/ACN solution.

![](_page_7_Figure_3.jpeg)

Figure 7. Switching times and % transmittance changes recorded at 1190 nm for PBIMN in 0.1M LiClO<sub>4</sub>-NaClO<sub>4</sub>/ACN solution between 0.0 V and 1.4 V.

![](_page_7_Figure_5.jpeg)

**Figure 8.** Percent transmittance change and switching times for 1:1 (BIMN:EDOT) copolymer monitored at 1370 nm in 0.1 M NaClO<sub>4</sub>–LiClO<sub>4</sub>/ACN electrolyte-solvent couple between -1.0 V and 1.4 V.

![](_page_8_Figure_2.jpeg)

Figure 9. Surface characteristics of (A) pristine PBIMN (B) Pristine PEDOT (C) P(BIMN–EDOT) and (D) P(BIMN–EDOT) (1:1 ratio) (with 100000 magnification) SEM images.

## Conclusions

In this study, a novel copolymer based on the BIMN and EDOT was successfully prepared by electropolymerization. With the presence of EDOT the electrochemical properties of the resulting polymers were greatly changed. Also, changes in the surface were proven by SEM technique. In literature, EDOT was generally preferred for copolymerization due to desired electrochemical properties. Results of this study also support this argument via improved properties such as: lower oxidation potential, lower optical bandgap and enhanced kinetic parameters. In the light of this knowledge, it can be stated that compare to pristine PBIMN, due to their electron rich character EDOT bearing copolymers reveal significant amendments in the optical properties.

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