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ABSTRACT

New solid biopolymer electrolytes (SBEs) were prepared by integrating stilbene-imine derivatives bearing vinylene (-CH=CH-) and azomethine (-CH=N-) as additives in carboxymethyl cellulose (CMC) based electrolyte. The investigation on their spectroscopic and theoretical assessments were conducted to alter the energy level in improving the structural and ionic conductivity performance. The simulated results from frontier molecular orbitals (FMO) and Mulliken-charge analysis revealed that $-CF_3$ and $-NO_2$ substituents significantly reduce the HOMO-LUMO gap up to 0.68 eV. The highest ionic conductivity of SBEs achieved at ambient temperature was $\sim 8 \times 10^{-3}$ Scm⁻¹ upon the addition of additive, obeying an Arrhenius model with reciprocal of temperature (303 K–373 K). The coordination interaction of C–O bond and CH=N band facilitated the dissociation of more cation (H⁺) of NH₄Cl which permits alternative route for H⁺ to hop into coordinating site in CMC. The outcomes are ideal in the development of electrochemical devices.

1. Introduction

Recently, the development of polymer electrolyte (PE) has attracted enormous interest both in academia and industry as it provides promising prospect in application of advanced electrochemical energy devices such as, dye-sensitized solar cell, supercapacitor, batteries, and sensors (Ngai, Ramesh, Ramesh, & Juan, 2016; Singh et al., 2016; Zhang, Liu, Cui, & Chen, 2015). In this context, PE plays an important building block components that can be utilized as ionic conductors (Ahmed & Abdullah, 2020; Youcef et al., 2020), separator in a battery for short circuit prevention (Yue et al., 2016; Zhang, Zhao et al., 2015) and regeneration of the oxidized dye molecules (Careem, Aziz, & Buraidah, 2017) which consequently affect the performance of the devices. Owing to this interest, many research works have been focused on the benefits of the modification with different approach and implementation of various type of PEs, including reviews on solid polymer electrolytes (SPEs) to attain good efficiencies and performances. For instance, (Kumaran et al., 2018; Tan, Ramesh, & Liew, 2019) studied the performance of electrochemical application for polymer electrolytes

based on different polymers such as poly(vinyl alcohol) (PVA), polyacrylamide-co-acrylic acid (PAAC), poly(ethylene oxide) (PEO) and to name a few. In recent years, Zhou, Shanmukaraj, Tkacheva, Armand, & Wang, 2019 reviewed the non-flammable electrolyte systems to include solid all-solid state for Li metal batteries.

In these sense, solid biopolymer electrolytes (SBEs) offer more practical and convenient to use over liquid and gel electrolytes which can give good mechanical stability, flexibility, lightweight, leakage free and higher operating temperature (Singh et al., 2016; Su'ait, Rahman, & Ahmad, 2015; Zhao et al., 2020). On top of that, the use of biodegradable polymers as polymer host in solid state electrolytes can ideally replace the harmful existing materials, owing good thermal and thin film formation abilities for green energy applications (Ahmed & Abdullah, 2020; Bella, Mobarak, Jumaah, & Ahmad, 2015). Among various biopolymer materials, the use of cellulose derivatives (Gupta & Varshney, 2019; Kostag, Gericke, Heinze, & El Seoud, 2019) namely chitosan, methylcellulose (MC) and carboxymethyl cellulose (CMC), carrageenan, pectin, chitin, lignocellulosic materials in electrolyte has received much attention since it possesses a wide variety of advantages

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such as having low density materials, high specific length film forming ability and exhibit biodegradable properties which can be used as SBEs. Noor & Isa, 2019; Samsudin & Saadiah, 2018 have developed and investigated new proton conducting biopolymer electrolytes based on carboxymethyl cellulose (CMC) doped with different ammonium salt for advanced materials application. The correlation between impedance approach, mechanism ionic conduction and dielectric parameter were also thoroughly described (Mazuki, Majeed, Nagao, & Samsudin, 2020; Zainuddin, Rasali, Mazuki, Saadiah, & Samsudin, 2020). Nevertheless, in-depth studies are still desired to optimize their performances due to their major drawbacks of low ionic conductivity which limits their practical technological applications and performance.

Alternatively, numerous approaches are attempted with the goal to enhance the ionic conductivity performance and sustain interior properties of SBEs including blending of polymers, incorporated filler, ionic liquid and additives/plasticizer into the polymer host matrix (Ambika et al., 2018; Chai & Isa, 2016; Yang et al., 2017). Within this interest, the incorporation of a small amount of other chemical species into the electrolyte composition becomes another promising alternative that can alter the structural stability and influence the SBEs performance (Karthika, Ganesan, Thomas, Rani, & Prakash, 2019). Based on previous literatures, 4-tertbutylpyridine (TBP), organic nitrogenous compound (Ganesan, Mathew, Paul, Maruthamuthu, & Suthanthiraraj, 2013), pyridine, thiourea (Pavithra, Velayutham, Sorrentino, & Anandan, 2017) and benzimidazole (Muthuraaman, Will, Wang, Moonie, & Bell, 2013) are some examples of small molecules employed in polymer electrolyte to improve the conductivity and efficiency of the system.

Regarding to this interest, the motivation which led to this contribution arises on the extensive studies involving organic additives in electrolytes based on semiconducting materials system. The devotions in

this present work is to examine the capability of conjugated π -systems of alkoxy stilbene-imine to act as additive in biopolymer-salt electrolyte on CMC doped with ammonium chloride (NH₄Cl) system. The coordination chemistry of hybrid moieties of vinylene (-CH=CH-) and azomethine (-CH=N-) exert a great deal in semiconducting properties as it possess extensive conjugated system which able to conduct electron through their π -system and can afford good charge transport to the polymer electrolyte matrix. On top of that, the uniqueness features of alkoxy stilbene-imine are ascribed by the existence of possible active site of C-O bond and CH=N band for alternative pathway for electron flow to biopolymer-salt electrolyte. Therefore, the involvement of hybrid moieties system of stilbene-imine was carried out in order to overcome the limitations inherent in a mixture of biopolymer-salt electrolyte. The evaluation on how far these types of molecular compounds can be able to improve ionic conductivity and alter structural of SBEs film was also intensively investigated. Within this interest, stilbene-imine based additives are expected to have good interaction with biopolymer-salt electrolyte that leads to the effective properties of ionic conductivity in SBEs system.

2. Experimental section

2.1. Materials

All chemicals, solvent and materials were used as received without further purification. 1-iodo-4-nitrobenzene, 4-iodoaniline, 4-vinylaniline and carboxymethyl cellulose (CMC, $M_w \sim 90,000$ g/mol) were purchased from Sigma-Aldrich, 4-cyanostyrene, 4-chlorostyrene, 4-vinylaniline, 4-(trifluoromethyl)styrene and methyl 4-iodobenzoate were provided by Acrós Organic. Whilst, ammonium chloride,



Scheme 1. The synthetic approach for the preparation of alkoxy stilbene-imine (3a-2C)-(3b-10C).

acetonitrile, ethanol, triethylamine, and tetrahydrofuran were obtained from Merck.

2.2. Instrumentations

CHN elemental analyses were acquired using FLASHEA 1112 CHNS analyzer. IR spectra were obtained from Perkin Elmer Spectrum 100 Fourier Transform Infrared Spectrometer in KBr pellets within the frequency region of 4000–400 cm⁻¹. The ¹H (400.11 MHz) and ¹³C (100.61 MHz) spectra were recorded on Bruker Avance III 400 Spectrometer with deuterated chloroform (CDCl₃) solvent and tetramethylsilane (TMS) as an internal standard. The density functional theory (DFT) calculation were analyzed via Gaussian 09 software package employing with basis set function of B3LYP/6-31 G (d,p). The electronic properties of HOMO-LUMO gap with corresponding absorption wavelengths were performed by time-dependent DFT (TD-DFT) method.

2.3. Synthesis of stilbene-imine as organic additive

All reactions and work up were performed under an ambient environment and no special precaution steps were taken during the synthetic work to eliminate air or moisture unless otherwise stated. In the synthetic work, stilbene-imine additive consists of three major steps which were begun with the preparation of precursors over aerobic condition of palladium-catalysed Heck cross-coupling reactions (1a-1b). Next, reactions were continued with the preparation of alkoxybenzaldehydes acting as another precursors (2a-2c) via Williamson ether synthesis with various alkyl bromide and 4-hydroxybenzaldehyde. Subsequently, precursors (1a-1b) were reacted with 2a-2c to yield the focal targeted compounds of stilbene-imine (3a-2C)-(3b-10C) derivatives via Schiff Base condensation reactions. Precursors (1a-1b and 2a-2c) only used to synthesize the stilbene-imine additives and did not involve directly in this study. Scheme 1 depicts the overall synthetic route applied in this work. The 3a-6C (additive- 2) has been prepared and reported at some extends in previous occasions (Rahamathullah & Khairul, 2018). Nevertheless, the study on the capability of this conjugated molecular system as organic additives have never been carried out although the existence of lone pair of electrons in oxygen and nitrogen atoms is expected to have interaction with polymer matrix which can enhance ionic conductivity of the electrolytes. Therefore, for this contribution, the influence of the synthesized additives (3a-2C)-(3b-10C) were investigated on the performance of CMC-biopolymer based electrolyte.

2.3.1. Synthesis of 4-[[(4-ethoxyphenyl)methylene]amino)]-4'-(trifluoromethyl)stilbene (3a-2C)-additive 1

An equimolar amount of 1a (0.50 g, 1.90 mmol) and 2a (0.29 g, 1.90 mmol) were dissolved in 50 mL of ethanol equipped with a Dean-Stark condenser. The mixture was then put at reflux with constant stirring at the solvent distillation temperature (79 °C) for ca. 6 h and monitored via TLC (hexane: ethyl acetate) (3:2). Upon completion, the solution was dried over anhydrous Na₂SO₄, filtered and cooled at room temperature. A pale yellow precipitate formed from the solution mixture were then filtered, collected and recrystallized from acetonitrile to obtain the yellow flakes of the title compound of **3a-2C** (0.63 g, 84 %). IR (KBr): ν (C–H aromatic) 3020 cm⁻¹; ν (C–H aliphatic) 2980 cm⁻¹, 2882 cm⁻¹; ν (C==C, vinyl) 1588 cm⁻¹; ν (C==C, aromatic) 1567 cm⁻¹ and 1511 cm⁻¹; ν (C=N)1604 cm⁻¹; ν (C-O, ether) 1166 cm⁻¹; ν (C-F) 841 cm⁻¹. ¹H NMR (400.11 MHz, CDCl₃): δ 1.39 (t, J = 7.0 Hz, 3H, CH₃); 4.03 (q, J =7.0 Hz, 2H, OCH₂); 6.92 (d, *J* = 8.8 Hz, 2H, Ar-H); 7.01–7.12 (d-d, 2H, HC=CH); 7.17 (d, *J*=8.4 Hz, 2H, Ar-H); 7.48 (d, *J* = 8.4 Hz, 2H, Ar-H); 7.54 (s, 4H, Ar-H); 7.77 (d, J = 8.8 Hz, 2H, Ar-H); 8.35 (s, 1H, NH). ¹³C NMR (100.61 MHz, CDCl₃): 8 13.72 (s, CH₃); 62.69 (s, CH₂-O); 129.60, 129.77 (2 x s, C=C); 128.03 (s, C-CF); 113.73, 120.43, 124.60, 124.64, 125.37, 125.46, 126.64, 133.11, 139.96, 151.28, 15856 ($12 \times s$, Ar); 160.82 (s, C=N). Elemental analysis for C₂₄H₂₀F₃NO: [Found (Calcd.)]: C = 72.90 (72.48); H = 5.10 (5.04); N = 3.54 (3.44). (See Supp. data S1,

S2, S3).

2.3.2. Synthesis of 4-[[(4-hexyloxyphenyl)methylene]amino)]-4'-(trifluoromethyl)stilbene (3a-6C)-additive 2

Yellow precipitate of (3a-6C) (0.73 g, 85 %) was synthesized from 1a (0.50 g, 1.90 mmol) and 2b (0.39 g, 1.90 mmol) in the same manner as described above. IR (KBr): ν (C–H aromatic) 3023 cm⁻¹; ν (C–H aliphatic) 2935 cm⁻¹, 2874 cm⁻¹; v(C=C, vinyl) 1585 cm⁻¹; v(C=C, aromatic) 1567 cm⁻¹ and 1511 cm⁻¹; ν (C=N) 1606 cm⁻¹; ν (C=O, ether) 1165 cm⁻¹; ν (C-F) 844 cm⁻¹. ¹H NMR (400.11 MHz, CDCl₃): δ 0.92 (t, J = 7.0Hz, 3H, CH₃); 1.26–1.85 (m, 8H, CH₂); 4.03 (t, *J* = 6.6 Hz, 2H, OCH₂); 6.99 (d, J = 8.4 Hz, 2H, Ar-H); 7.08–7.22 (d-d, 2H, HC=CH); 7.24 (d, *J*=8.4 Hz, 2H, Ar-H); 7.55 (d, *J* = 8.4 Hz, 2H, Ar-H); 7.60 (s, 4H, Ar-H); 7.84 (d, J = 8.8 Hz, 2H, Ar-H); 8.42 (s, 1H, NH). ¹³C NMR (100.61 MHz, CDCl₃): δ 13.00 (s, CH₃); 21.58, 24.67, 28.13, 30.55 (4 x s, CH₂); 67.24 (s, CH₂-O); 129.58, 129.75 (2 x s, C=C); 127.94 (s, C-CF); 113.74, 120.44, 124.60, 124.63, 125.35, 125.46, 126.63, 133.08, 139.96, 151.29, 158.59 (12 \times s, Ar); 161.03 (s, C=N). Elemental analysis for C₂₈H₂₈F₃NO: [Found (Calcd.)]: C = 74.48 (73.88); H = 6.25 (5.74); N = 3.10 (2.89). (See Supp. data S4, S5, S6).

2.3.3. Synthesis of 4-[[(4-decyloxyphenyl)methylene]amino)]-4'-(trifluoromethyl)stilbene (3a-10C)-additive 3

Yellow precipitate of (3a-10C) (0.83 g, 86 %) was synthesized from 1a (0.50 g, 1.90 mmol) and 2c (0.50 g, 1.90 mmol) in the same manner as described above. IR (KBr): ν (C–H aromatic) 3022 cm⁻¹; ν (C–H aliphatic) 2919 cm⁻¹, 2875 cm⁻¹; v(C=C, vinyl) 1587 cm⁻¹; v(C=C, aromatic) 1570cm⁻¹ and 1511 cm⁻¹; v(C=N) 1607 cm⁻¹; v(C-O, ether) 1166 cm⁻¹; ν (C-F) 847 cm⁻¹. ¹H NMR (400.11 MHz, CDCl₃): δ 0.89 (t, J = 6.8 Hz, 3H, CH₃); 1.26–1.85 (m, 8H, CH₂); 4.03 (t, J = 6.4 Hz, 2H, OCH₂); 6.99 (d, J = 8.8 Hz, 2H, Ar-H); 7.08–7.22 (d-d, 2H, HC=CH); 7.24 (d, *J*=8.4 Hz, 2H, Ar-H); 7.55 (d, *J* = 8.4 Hz, 2H, Ar-H); 7.61 (s, 4H, Ar-H); 7.84 (d, J = 8.4 Hz, 2H, Ar-H); 8.42 (s, 1H, NH). ¹³C NMR (100.61 MHz, CDCl₃): *δ* 14.13 (s, CH₃); 22.69, 26.02, 29.18, 29.33, 29.39, 29.56, 29.58, 31.91 (8 \times s, CH₂); 68.25 (s, CH₂-O); 126.37, 126.48 (2 x s, C=C); 127.66 (s, C-CF); 114.75, 121.47, 125.62, 125.65, 127.66, 128.88, 130.62, 130.73, 134.11, 151.29, 159.66 ($12 \times s$, Ar); 162.05 (s, C=N). Elemental analysis for C₃₂H₃₆F₃NO: [Found (Calcd.)]: C = 75.71 (75.18); H = 7.15 (7.74); N = 2.76 (2.89). (See Supp. data S7, S8, S9).

2.3.4. Synthesis of 4-[[(4-ethoxyphenyl)methylene]amino)]-4'nitrostilbene (3b-2C)-additive 4

Yellow precipitate of (**3b-2C**) (0.68 g, 88 %) was synthesized from **1b** (0.50 g, 2.08 mmol) and **2a** (0.31 g, 2.08 mmol) in the same manner as described above. IR (KBr): ν (C–H aromatic) 3234 cm⁻¹; ν (C–H aliphatic) 2985 cm⁻¹ and 2875 cm⁻¹; ν (C=C, vinyl) 1582 cm⁻¹; ν (C=C, aromatic) 1560 cm⁻¹ and 1515 cm⁻¹; ν (C=C, vinyl) 1582 cm⁻¹; ν (C=C, aromatic) 1604 cm⁻¹; ν (C–O, ether) 1163 cm⁻¹. ¹H NMR (400.11 MHz, CDCl₃): δ 1.39 (t, J = 7.0 Hz, 3H, CH₃); 4.03 (q, J = 7.0 Hz, 2H, OCH₂); 6.92 (d, J = 8.8 Hz, 2H, Ar-H); 7.04–7.24 (d-d, 2H, HC=CH); 7.17 (d, J=8.0 Hz, 2H, Ar-H); 7.57 (d, J = 8.8 Hz, 2H, Ar-H); 8.14 (d, J = 8.8 Hz, 2H, Ar-H); 8.35 (s, 1H, NH). ¹³C NMR (100.61 MHz, CDCl₃): δ 13.72 (s, CH₃); 62.69 (s, CH₂-O); 126.95, 127.90 (2 × s, C=C); 113.72, 120.53, 123.16, 124.46, 125.71, 129.65, 131.88, 132.58, 143.01, 145.62, 151.78, 158.79 (12 × s, Ar); 160.88 (s, C=N). Elemental analysis for C₂₃H₂₀N₂O₃: [Found (Calcd.)]: C = 74.18 (74.74); H = 5.41 (5.74); N = 7.52 (7.13). (See Supp. data S10, S11, S12).

2.3.5. Synthesis of 4-[[(4-hexyloxyphenyl)methylene]amino)]-4'nitrostilbene (3b-6C)-additive 5

Yellow precipitate of (**3b-6C**) (0.78 g, 87 %) was synthesized from **1b** (0.50 g, 2.08 mmol) and **2b** (0.43 g, 2.08 mmol) in the same manner as described above. IR (KBr): ν (C–H aromatic) 3234 cm⁻¹; ν (C–H aliphatic) 2920 cm⁻¹, 2852 cm⁻¹; ν (C=C, vinyl) 1583 cm⁻¹; ν (C=C, aromatic)

1561 cm⁻¹ and 1519 cm⁻¹; ν (NO₂) 1424 cm⁻¹ and 1340 cm⁻¹; ν (C—N) 1605 cm⁻¹; ν (C—O, ether) 1163 cm⁻¹. ¹H NMR (400.11 MHz, CDCl₃): δ 0.85 (t, J = 7.0 Hz, 3H, CH₃); 0.84–1.78 (m, 8H, CH₂); 3.96 (t, J = 6.6 Hz, 2H, OCH₂); 6.92 (d, J = 8.8 Hz, 2H, Ar-H); 7.04–7.24 (d-d, 2H, HC=CH); 7.17 (d, J=8.4 Hz, 2H, Ar-H); 7.50 (d, J = 8.4 Hz, 2H, Ar-H); 7.57 (d, J = 8.8 Hz, 2H, Ar-H); 7.77 (d, J = 8.4 Hz, 2H, Ar-H); 8.14 (d, J = 8.8 Hz, 2H, Ar-H); 8.34 (s, 1H, NH). ¹³C NMR (100.61 MHz, CDCl₃): δ 13.00 (s, CH₃); 21.57, 24.67, 28.12, 30.55 (4 × s, CH₂); 67.25 (s, CH₂-O); 126.95, 127.85 (2 × s, C=C); 113.76, 120.54, 123.17, 124.47, 125.72, 129.65, 131.89, 132.59, 143.03, 145.64, 151.80, 158.82 (12 × s, Ar); 161.12 (s, C=N). Elemental analysis for C₂₇H₂₈N₂O₃: [Found (Calcd.)]: C = 75.68 (75.74); H = 6.59 (5.74); N = 6.54 (7.13). (See Supp. data S13, S14, S15).

2.3.6. Synthesis of 4-[[(4-decyloxyphenyl)methylene]amino)]-4'nitrostilbene (3b-10C)-additive 6

Yellow precipitate of (3b-10C) (0.86 g, 85 %) was synthesized from 1b (0.50 g, 2.08 mmol) and 2c (0.55 g, 2.08 mmol) in the same manner as described above. IR (KBr): ν (C–H aromatic) 3234 cm⁻¹; ν (C–H aliphatic) 2920 cm⁻¹, 2852 cm⁻¹; v(C=C, vinyl) 1583 cm⁻¹; v(C=C, aromatic) 1561 cm⁻¹ and 1519 cm⁻¹; ν (NO₂) 1424 cm⁻¹ and 1340 cm^{-1} ; ν (C=N) 1605 cm^{-1} ; ν (C-O, ether) 1163 cm^{-1} . ¹H NMR (400.11 MHz, CDCl₃): δ 0.82 (t, *J* = 6.8 Hz, 3H, CH₃); 1.18–1.78 (m, 16H, CH₂); 3.96 (t, J = 6.6 Hz, 2H, OCH₂); 6.92 (d, J = 8.4 Hz, 2H, Ar-H); 7.03–7.23 (d-d, 2H, HC=CH); 7.17 (d, J=8.4 Hz, 2H, Ar-H); 7.50 (d, J = 8.4 Hz, 2H, Ar-H); 7.57 (d, J = 8.8 Hz, 2H, Ar-H); 7.77 (d, J = 8.4 Hz, 2H, Ar-H); 8.14 (d, J = 8.8 Hz, 2H, Ar-H); 8.34 (s, 1H, NH). ¹³C NMR (100.61 MHz, CDCl₃): δ 13.08 (s, CH₃); 21.66, 25.00, 28.16, 28.30, 28.36, 28.53, 28.55, 30.88 (8 x s, CH₂); 67.26 (s, CH₂-O); 126.95, 127.88 (2 \times s, C=C); 113.77, 120.54, 123.16, 124.47, 125.72, 129.64, 131.91, 132.59, 143.03, 145.66, 151.84, 158.79 (12 \times s, Ar); 161.12 (s, C=N). Elemental analysis for $C_{31}H_{36}N_2O_3$: [Found (Calcd.)]: C = 76.83 (76.14); H = 7.49 (6.74); N = 5.78 (5.13). (See Supp. data S16, S17, S18).

2.4. Computational method: DFT studies

The theoretical studies were evaluated through Gaussian 09

quantum mechanical software employing DFT approach with basis set of B3LYP/6-31 G (d,p). The energy separation between HOMO and LUMO, frontier molecular orbital (FMO) and the corresponding absorption wavelengths were performed by time-dependent density functional theory (TD-DFT). The molecular geometry optimization was employed using polarizable continuum model (PCM) with the integral equation formalism variant (IEF-PCM) in dichloromethane solvent.

2.5. Preparation of solid biopolymer electrolyte (SBEs) Film

An amount of 2.0 g of carboxymethyl cellulose (CMC) powder was dissolved in 100 mL of distilled water and stirred constantly for *ca.* 12 h at ambient environment. The amount of 16 wt.%, 0.38 g of ammonium chloride (NH₄Cl) was added into CMC solution and stirred for another *ca.* 5 h until completely homogenous. The amount of ammonium salt used in this work was fixed which referred to the highest conductivity of CMC-NH₄Cl that was reported in previous literature (Ahmad & Isa, 2016), in order to use this previously developed system as reference before adding our synthesized additive. The homogenous solution was then casted into glass petri dishes and dried in an oven at 55 °C for *ca.* 30 h to allow CMC-NH₄Cl film to form. The SBEs were kept in desiccators for further drying prior being characterized to ensure the removal of residual moisture in the film.

2.5.1. Preparation of SBEs containing stilbene-imine as additive

An amount of 1 milliMolar (mM) of synthesized stilbene-imine was dissolved in 5 mL organic solvent. Then, the solution was added dropwise into CMC-NH₄Cl solution with constant stirring to form clear homogenous dissolution. In this work, only 1 mM of stilbene-imine was used as additives in order to avoid phase separation and form clear film due to the effect of alkoxy chain and aromatic group that can form heterogeneous mixture in water and form non-uniform film. The preparation of CMC-NH₄Cl was carried out in the same manner as described in 2.5. Then, the solution was casted into glass petri dishes and heated in an oven at 55 °C for *ca*. 30 h to allow film to form. The SBEs were then transferred into desiccator for extended the drying process for solvent evaporation purpose. Fig. 1 illustrates the stepwise preparation of SBEs in this study and compositions of CMC-NH₄Cl-(stilbene-imine) coded as



Fig. 1. Schematic diagram of SBEs preparation.

Table 1

Frontier molecular orbitals (FMOs) of stilbene-imine additives.



F(3a-2C)-F(3b-10C).

2.6. SBEs characterization

2.6.1. Fourier transform infrared (FT-IR) spectroscopy

The structural and intermolecular interaction of the developed SBEs have been examined via FTIR spectra on Thermo Nicolet 380 FTIR spectrometer equipped with an Attenuated Total Reflection (ATR) mode within the vibration frequency ranging from 4000 to 450 cm⁻¹.

2.6.2. Electrical impedance spectroscopy (EIS)

For ionic conductivity characterization, the SBE samples were evaluated via EIS using HIOKI LCR Hi Tester (model 3532–50) at varies frequency range between 50 Hz to 1 MHz. The samples were cut into a fitting size of small discs with 2 cm diameter and sandwiched between blocking stainless steel electrodes of the sample holder which connected to the LCR tester. The ionic conductivity, σ was calculated using the relation in following equation (Shukur & Kadir, 2015).

$$\sigma = \frac{t}{R_b A} \tag{1}$$

From the equation, t (cm) is the thickness of the sample, A (cm²) is the surface area of electrode-electrolyte contact area of SBE and R_b is bulk resistance obtained from plotting the negative imaginary impedance (- Z_i) versus real part (Z_r) of impedance.

3. Results and discussion

3.1. Computational detailed on stilbene-imine additives

The frontier molecular orbital (FMOs) of all additives along with their respective $\Delta E_{HOMO-LUMO}$ energy values in eV are depicted in Table 1. The energy gap between HOMO and LUMO for stilbene-imine

additives is found to be at around 3.49 eV - 3.07 eV. This value explains the eventual charge transfer interaction with the molecule where $-CF_3$ substituent has slightly large HOMO-LUMO gap which reflects low chemical reactivity and high kinetic stability compared to $-NO_2$ substituent. Nonetheless, in overall results, we can conclude that the HOMO-LUMO gaps of both series are comparatively small and fall in the range of semiconducting materials. The low HOMO-LUMO energy gaps of additives indicate the molecule are soft and also possess higher thermal and kinetic stabilities according to softness-hardness rule. From

Table 2

The excitation energy, oscillator strengths (f) and major contributions of the transitions from ground state (S_0) to excited states (S_n).

Molecule	Electronic transition	Wavelength		Oscillator	Major
		Exp	Cal	strength	contribution (in %)
Additive 1	$S_0 \rightarrow S_1$	360	401	1.8743	H→L (98)
Additive 2	$S_0 \rightarrow S_1$	360	401	1.8991	H→L (98)
Additive 3	$S_0 \rightarrow S_1$	360	401	1.8758	H→L (98)
Additive	$S_0 \rightarrow S_1$	-	475	1.3296	H→L (99)
	$S_0 \rightarrow S_2$	396	373	0.3423	H-1→L (73)
4					H→L+1 (24)
	$S_0 \rightarrow S_3$	293	359	0.2834	H-1→L (26)
					$H\rightarrow L+1(71)$
Additive 5	$S_0 \rightarrow S_1$	-	475	1.3449	H→L (99)
	$S_0 \rightarrow S_2$	396	373	0.3436	H-1→L (74)
					H→L+1 (23)
	$S_0 \rightarrow S_3$	293	359	0.3015	H-1→L (25)
					H→L+1 (72)
Additive 6	$S_0 \rightarrow S_1$	396	451	1.5114	H→L (99)
	$S_0 \rightarrow S_2$	293	360	0.3772	H-1→L (74)
					H→L+1 (23)

Table 3

Value of squared effective charges (-Ln χ^2) of all carbon atoms in the aromatic ring of substituted stibene-imine additives.



the FMO distribution, the filled π -orbital (HOMO) and unfilled anti π -orbital (LUMO) are delocalized throughout the entire molecule including aromatic rings, trans-stilbene and double bonds of --CH=Nmoiety except alkoxy chain length. The alkoxy chains length had no significant effect and did not show much different on the distribution of electronic clouds in FMOs even though electron donating (ED) effect becomes stronger with increasing alkoxy chain lengths to the conjugated backbone. In contrast, by further tuning of electron withdrawing (EW) substituents namely -CF₃ and -NO₂ of stilbene-imine additive, the charge distribution of the HOMO was slightly shifted downwards around 0.13 eV - 0.43 eV and LUMO within the range 0.14 eV - 0.85 eV. These indicate that mesomeric effect and EW strength capability shows a crucial role in the variations of energy level. In these sense, we can see that the EW group stabilizes LUMO energy level more than its HOMO energy level. In conclusion, the changes in HOMO and LUMO values resulted in the narrower band gap due to the effect of EW substituent and hence lowering the HOMO-LUMO energy gap.

Additionally, the charge density of FMO for stilbene-imine additive was evaluated in order to examine the nature of major electronic transition upon photoexcitation (Daengngern & Kungwan, 2015). In this case, the HOMO and LUMO are assigned to π and π^* character and main contribution are summarized in Table 2. Considering TD-DFT calculation, it can be said that the electron density contribution of all additives



Fig. 2. Cole-Cole plot for impedance diagram of $CMC-NH_4Cl$ electrolyte and various $CMC-NH_4Cl$ -(stilbene-imine) SBEs. The inset shows the enlargement of the SBEs at high frequency part.

Table 4

Thickness, bulk resistance and ionic conductivity of all SBEs involved in this study.

SBEs	Thickness, t (cm)	Bulk Resistance, $R_{\rm b}\left(\Omega\right)$	Conductivity, σ (S/cm ⁻¹)				
References							
CMC-	0.015	2.82	1.69×10^{-3}				
NH ₄ Cl							
Trifluoromethyl (CF ₃) series							
F(3a-2C)	0.017	0.94	$5.76 imes10^{-3}$				
F(3a-6C)	0.018	0.78	$7.34 imes10^{-3}$				
F(3a-10C)	0.018	0.69	$8.30 imes 10^{-3}$				
Nitro (NO ₂) series							
F(3b-2C)	0.018	0.90	6.37×10^{-3}				
F(3b-6C)	0.018	0.81	$7.07 imes 10^{-3}$				
F(3b-10C)	0.017	0.61	8.86×10^{-3}				

are predominantly arises from H→L (98–99 %) with high oscillator strength (f > 1.5) in first excited singlet state $S_0 \rightarrow S_1$. While, the evident that excited singlet state $S_0 \rightarrow S_2$ attributed to HOMO-1→LUMO (72–74 %) and HOMO→LUMO+1 (23–25 %) configuration corresponds to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions as tabulated in Table 2. Nonetheless, the contribution of excited singlet states $S_0 \rightarrow S_3$ for is sizably reduced by small calculated oscillator strength (f < 0.4) and nearly forbidden and undetectable for considerations. As an overall result, the resulting calculated λ_{max} is in good agreement with the experimental value where significantly red shifted occurred due to the superposition of the bath-ochromic shift and effect of the conjugation targeted system.

From computational study, it was revealed that different substituents of stilbene-imine additives can influence the ionic conductivity performance of SBEs system where it can be correlated with the energy band gap (HOMO-LUMO). In this sense, to determine the correlation between the substituents of stilbene-imine additive with the conductivity, effective squared charges (χ^2) followed by –Ln χ^2 for the aromatic rings in the stilbene-imine derivatives were calculated at the theoretical level of B3LYP/6-31 G (d,p) as depicted in Table 3. The χ^2 on the α th atom can contribute to the prediction of the vibrational intensities, reaction pathway and conductivity properties which can give consistent results with the experimental approach (Ghazali, Kubulat, Isa, Samsudin, & Khairul, 2014; Person & Kubulat, 1990). Surprisingly, the sequence of total Ln χ^2 value particularly for the third ring of stilbene-imine additives were exactly in the same order with experimental outcomes of conductivities. The trends of the sequences are depending on the electronegativity of electron withdrawing group that attached to the ring system namely CF₃ < NO₂. It revealed that the conductivity depends much on the delocalization of the phenyl ring system of the



Fig. 3. Temperature-dependence of ionic conductivity of CMC-NH₄Cl electrolyte and CMC-NH₄Cl-(stilbene-imine) SBEs.

stilbene-imine derivatives. Indeed, the value of higher squared effective charges (Ln χ^2) could be explained by the conjugation length and delocalization of π -electrons along the molecule. From the promising result of energy band gap (E_g) and effective charges (χ^2) of the stilbene-imine compounds via theoretical study and experimental result obtained, these candidates revealed great potential to act as additives in SBE for optoelectronic application.

3.2. Ionic conductivity

The addition of additives in biopolymer-salt electrolytes is potentially would enhance the conductivity performance. Hence to investigate the influence of incorporation stilbene-imine additives on the conductivity behaviour in SBEs system, highest conducting CMC-NH4Cl in the salted system (16 wt. %) was used as a reference (Ahmad & Isa, 2016) for this type of work. In this case, the conductivity value for CMC-NH4Cl electrolyte was identified at $1.69\times 10^{-3}\,\text{Scm}^{-1}$ which is in comparable with reported results by Ahmad and Isa, 2016. On top of that, the conductivity results increase gradually upon the addition of stilbene-imine additives into CMC-NH4Cl electrolyte within the range of $5.76\times 10^{-3}\,\text{Scm}^{-1}$ to $8.86\times 10^{-3}\,\text{Scm}^{-1}$ at room temperature (303 K) as depicted in Fig. 2. The enhancement in conductivity for CMC-NH₄Cl-(stilbene-imine) SBEs can be ascribed due to the decrease of bulk resistance (*R*_b) in the system as illustrated in Cole-Cole plot (Fig. 2). The summarized data for the obtained conductivity (σ) and bulk resistance $(R_{\rm b})$ is presented in Table 4.

The results indicate that the additives with -CF3 and -NO2 electron withdrawing groups revealed enhancement in conductivity based on their electronegativity and substitutions group on the additives. This occurrence can be correlated to the increment of ionic conductivity in which inferring information on the interaction between biopolymer-salt electrolyte and additive increases of ion dissociation and number of charge carriers of free ions (H⁺) (Alias, Chee, & Mohamad, 2017; Hafiza & Isa, 2017a, 2017b). The existence of nitrogen in (CH=N) moiety with electron donating and withdrawing group at the additives boost up the mobility of ion for the SBEs system (Ganesan et al., 2013; Karthika et al., 2019). Moreover, the conductivity values SBE are slightly increased with an increasing of alkoxy chain length by tuning the electron withdrawing group substitutions which follows the order (F(3a-2C) < (F (3a-6C) < (F(3a-10C) < (F(3b-2C) < (F(3b-6C) < (F(3b-10C) and affect the performance on the conductivity. Overall, the -NO2 series with decyloxy chain of additives give the highest value in conductivity in which confirms the electron substitution plays a crucial role in the performance of conductivity and electron flow of the molecule in SBEs system. Remarkably, the increments of conductivity in SBEs are in the line with HOMO-LUMO results and Mulliken charged obtained from



Fig. 4. Infrared spectra of SBE of CMC-NH₄Cl with stilbene-imine additives.

computational study.

3.3. Temperature-dependent ionic conductivity

To further investigate the ionic conduction mechanism and verify that SBEs was not affected from water content towards the enhancement of ionic conductivity, all the SBEs system were measured with a function of temperature. Fig. 3 portrays the temperature dependence plot of variation of log conductivity with reciprocal temperature in the range from 303 K to 373 K. The ionic conductivity noticeably increases monotonically with increasing temperature for all SBEs sample. Notably, the temperature-dependence conductivity in Fig. 3 were found to be in straight line with regression (R^2) values fit to ~1 and this linearity obeys thermal activated–Arrhenius relationship (Hafiza & Isa, 2018; Hashmi, Kumar, Maurya, & Chandra, 1990).

In this sense, the increment of conductivity with increasing temperature due to the factors of enhancement in ionic mobility through polymer chain and consequently increases the fraction of free volume at higher temperature facilitates the ions to hop between adjacent coordination sites (Moniha, Alagar, Selvasekarapandian, Sundaresan, & Boopathi, 2018; Selvakumar, Kalaiselvimary, Rajendran, & Prabhu, 2016). The presence of stilbene-imine additives in CMC-NH₄Cl electrolyte exhibits an enhancement in conductivity, indicate that additives assist in salt dissociation and lead to high mobility and conductivity as the temperature increases. Remarkably, the conductivity values of all SBEs system did not show any abrupt changes throughout the heating process which confirmed that ionic conductivity did not affect by water content, but attributed from the increment in mobility of charge carrier from doping salt and additives (Sim, Yahya, & Arof, 2016).

3.4. Biopolymer-salt-additive interactions study

The interactions of ions in electrolyte system can be determined by observing the changes of peak intensity, presence/or absence of new peak and shifting in the vibrational mode of molecules which provide crucial structural details of the polymer-salt with additives in IR analysis (Hafiza & Isa, 2017a, 2017b; Shukur, Ithnin, Illias, & Kadir, 2013). In this sense, the interaction of pure CMC, CMC-NH₄Cl electrolyte with/-without the addition of organic additives were analysed using FTIR. The





Fig. 5. Proposed interaction of biopolymer-salt with stilbene-imine additives of SBE system.

vibrational modes of O—H stretching, carboxylate (COO—) anions of (C=O) and glycosidic group (C=O–C) of CMC have been shifted in wavenumbers after addition of salt suggesting that the interaction and complexation have occurred in the biopolymer-salt of CMC-NH₄Cl system. The obtained findings were in same arguments with previous reported literatures on biopolymer-salt electrolyte system (Ahmad & Isa, 2016; Shukur & Kadir, 2015).

In contrast, noticeable changes of peak intensity and wavenumber of certain vibrational mode were detected before and after inclusion of additives and these have proven the interaction between biopolymersalt and additive occurred within the system as depicted in Fig. 4. Nevertheless, it revealed that the main functional groups of synthesized stilbene-imine additives disappeared and the characteristic of IR stretching bands of new SBEs were obviously related to the vibration mode of CMC-NH₄Cl electrolyte film (Karthika et al., 2019). This occurrence is due to the interruption of amorphous nature by incorporation of CMC-NH₄Cl electrolyte to form new SBEs film. The broadness and wavenumber of O-H band of the resulted CMC-NH4Cl-(stilbene-imine) SBEs were slightly shifted to higher wavenumbers within the range of 3360 cm^{-1} – 3375 cm^{-1} . This shift indicated that the presence of inter- and intramolecular hydrogen bonds acting on the --OH groups and free proton of dissociation of doping salt for SBE system. Meanwhile, the small hump at 2916 cm⁻¹ ascribed to aliphatic C—H stretching in CMC-NH₄Cl was shifted within the range of 2914 cm^{-1} – 2920 cm^{-1} upon the addition of stilbene-imine additives. In these sense, the wavenumbers of aliphatic C-H stretch for SBEs were decreased consistently with an increasing of chain length due to an increasing of van der Waals interaction between the alkoxy chains in additives. Additionally, the intensity and wavenumber of asymmetric stretching carboxylate (COO—) anions of (C==O) bands shifted from 1597 cm⁻¹ to the range of 1586-1593 cm⁻¹ respectively. In the case of C-O-C stretching band of glycosidic linkages, the SBEs with and without additives absorbed in the same IR energy at around 1416 cm^{-1} - 1425 cm⁻¹, nevertheless this peak became more intense with medium to strong intensity with the presence of additives. These related peaks are anticipated to be effected due to the lone pair electrons of oxygen on the C=O that interact with the stilbene-imine system.

The changes in wavenumber and intensity peak of SBE system revealed that additives have played a vital role in term of H⁺ dissociation of doping salt. In this context, the interaction between H⁺ and C=O group form a weak bond in which created alternative pathways for H⁺ to hop into coordinating site in CMC as illustrated in Fig. 5. The occurrence infers that the addition of stilbene-imine additives in CMC-NH₄Cl electrolyte can assist as an alternative transfer site for ion conduction of H⁺ from NH₄Cl towards C=O of the carboxyl group in CMC for SBEs system. This is due to the C–O band of ether from alkoxy and CH=N band from imine in stilbene-imine additives would help in dissociating more cation (H⁺) of NH₄Cl and attached to form weak bonding. The finding was in good agreement with previous studies where the additive molecules (in their respective work using ethylene carbonate) can create new pathways for ions to jump within the biopolymer host (Samsudin & Saadiah, 2018).

3.5. Conclusion

In summary, stilbene-imine additives have been successfully integrated into biopolymer-salt electrolyte as newly developed SBE via solution-casting technique. The incorporation of these additives in electrolytes boosts up the performance of the SBE by its excellent ionic mobility, dissociation of salt and conductivity. The substituent of the additives affected the conductivity of the electrolyte due to its HOMO-LUMO gap and effective charges (χ^2) of the aromatic portion. The highest conductivity at ambient temperature (303 K) achieved 8.86 × 10⁻³ Scm⁻¹ for the system containing -NO₂ substituted stilbene-imine additives. The temperature dependence ionic conductivity studies also indicated that SBEs obeys an Arrhenius model within the temperature

range of 303 K - 373 K. Thus, the outcome results revealed that the small change in conductivity upon addition of organic additives indicate that these promising candidates could provide efficient charge transport pathways in SBEs which leads to improvement in optoelectronic application.

CRediT authorship contribution statement

Rafizah Rahamathullah: Methodology, Data curation, Visualization, Writing - original draft. Wan M. Khairul: Supervision, Conceptualization, Writing - review & editing, Validation. M.I.N Isa: Supervision, Writing - review & editing, Validation.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.carbpol.2020.116935.

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