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Novel indole-based photosensitizers coupled with PEG-HEC quasi-solid-state electrolyte to improve energy conversion and stability of organic dyes based-dye sensitized solar cells



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ABSTRACT

A series of novel Indole based organic dyes were synthesized and coupled with a Poly-ethylene glycol-Hydroxy ethyl cellulose quasi-solid-state-electrolyte (PEG-HEC QSSE) polymer blended iodine electrolyte to obtain a metal-free dye-based dye-sensitized solar cell (DSSCs) with better stability. The newly synthesized organic dyes were confirmed through ¹H, ¹³C NMR, CHN analysis. The optical and electrochemical properties of the dyes were determined using UV-visible spectrometry and cyclic voltammetry techniques. A quasi-solid state (QSS) blended polymer PEG-HEC with iodide redox couple as electrolyte was characterized via Field emission Scanning Electron microscope (FE-SEM), UV-visible spectroscopy, XRD and DSC. A foremost comparative study was analysed on DSSC devices with the newly synthesised organic dyes (DPC, DTC, DPCY, DTCY, DPTCY and DTTCY) coupled with the QSSE. The electrochemical impedance spectrum was discussed for all the six dyes coupled with PEG-HEC QSSE, among that DTTCY sensitized device exhibits good ionic conductivity (1.13×10^{-3} S cm⁻¹), high chemical capacitance $(C_u=17.01 \ \mu\text{F})$, high recombination resistance (53.97 Ω) and lower charge transfer resistance (2.35 Ω) due to the presence of a strong electron-withdrawing group in the organic dye and also QSS behaviour of electrolyte. The longer electron lifetime (τ_n -58.51 ms) and better diffusion coefficient (4.25 × 10⁻⁷ cm² s^{-1}) of the device prove the short circuit current (J_{sc} = 16.39 mA cm⁻²) and enhancement of power conversion efficiency (PCE) of 6.24 % with better stability under AM 1.5 G illumination (100 mW cm⁻²). The combination of new Indole based organic dyes with PEG-HEC QSSE paved a way to improve the PCE and stability of organic dyes based DSSCs.

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1. Introduction

In the current scenario, energy utilisation in human life is a significant part and there is a demand for available resources. Solar energy is one of the clean, renewable resource, eco-friendly and thus played as alternative energy compared to all other traditional resources.[1] Among other photovoltaic technologies today researchers are emerging towards DSSCs as an alternate for siliconbased solar cell technologies.[2] DSSCs also termed as photoelectrochemical solar cell, where photo-induced reaction held on semiconducting electrode through an electrochemical modulate cell.[3] DSSCs show advantages in utilising solar energy to convert it to electrical energy at low-cost, simple fabrication, the ambient condition is enough to harvest energy and environment-friendly character under indoor and outdoor conditions.[4] The structure of

* Corresponding author. E-mail address: ganesans2@srmist.edu.in (S. Ganesan). the DSSCs is a sandwich-like structure comprised of working electrode, electrolyte and counter electrode. In general, DSSCs works upon illumination of solar light, initially, the dye molecules got excited by absorbing photons and the excited electrons have injected into the conduction band of the semiconducting surface (photoanode). The transported electrons flow to the counter electrode (usually platinum coated on the conductive substrate) through the external circuit. At this juncture, the oxidation-reduction reactions also happened in the electrolyte mediator that contains R/R⁺ redox couple. Through the redox reactions of the electrolyte, the electrons were shuttled back to the oxidized dye molecules and retaining the oxidised dye to its original state and these processes take place vice versa as a cycle [5].

The overall device performance mainly depends on the photons absorbed by the dye molecules. (e.g., Natural dyes, metal complex dye, organic metal-free dyes). [6,7,8] The light-harvesting sensitizer induces the photocurrent, with a low energy gap and suitable energy level for the electron injection process. [9] Nevertheless, metal complex dyes are lack in commercial application due to the less availability in nature and cost-effective. On the other hand, metalfree organic photosensitizers receive a huge interest and achieve a maximum PCE of 14 % by using a co-sensitizer. [10,11,12] A pushpull concept on the organic dyes readily shifts highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy level, which should match the redox potential of electrolyte and conduction band of photo-anode (TiO₂), which facilitate a dye regeneration and electron injection.

The organic small molecules with Donor-Acceptor (D-A) combination hold some excellent characteristics and intrinsic property like molar extinction coefficient (ε), internal charge transfer (ICT), low molecular weight, polarizability and structural tenability. The D-A system generally configures as D- π -A structure (i.e., Donor-spacer-Acceptor) that makes some special interest due to the following characteristics. (i) Facile and versatile in synthetic approaches, (ii) absorption wavelength can be shifted via structural modifications and (iii) capable of photo-induced charge separation. Meanwhile, the metal free-organic dyes will facilitate an intense light absorption, high extinction coefficient, rigidity and steric hindrances. They performed as a photo-anode after adsorbed on TiO₂ and allows the injection of photo-excited electrons [13,14,15]. The D-A system played a vital role in device performance by modification in molecular structure with different moiety to fine-tune energy level and kinetic properties of sensitizers [16,17,18].

In DSSCs huge number of $D-\pi-A$) the framework has used as metal-free organic dye sensitizers ([19,20]. The optoelectronic property of the $(D-\pi-A)$ system possesses a wide light-absorbing capacity due to its donor moiety and the π -conjugation spacer significantly alters the HOMO-LUMO energy level which facilitates the charge transfer. [21] The acceptor moiety binds on semi-conductor surface and transfer charge during electron injection [22,23]. While altering the $(D-\pi-A)$ systems the performance DSSCs was altered and improved [24]. The incorporation of additional electron-rich and electron-deficient moiety into the $(D-\pi-A)$ system results in efficient internal charge transfer, alter the absorption spectrum (redshift) and increased open-circuit voltage (V_{oc}) [25,26]. The extension of the π -conjugation bridge provides an effectual molar extinction coefficient (ϵ) and better electron delocalization. [27]

In this work, we designed and synthesized a series of novel Indole based organic dyes in $(2D-\pi-D'-A)$ and $(2D-\pi-D'-A-\pi-A)$ system that provides low lying band-gap and favourable molecular energy levels to enhance the PCE of DSSCs. The molecular engineering of $(2D-\pi-D'-A)$, $(2D-\pi-D'-A-\pi-A)$ arrangement involves (bis-N, N'-dimethylaniline unit is an isolated Group (IG) and a planar structure. The molecular stretch between two conjugated units via phenyl and thienyl group will result in excellent chargetransfer properties and red-shifted absorption [28]. Further improvement in charge mobility, electron delocalization by indole moiety, holding nitrogen atom as lone pair into the π -conjugated system [29] and pushes the electrons towards acceptor end. The effective charge separation acquired through electron-deficient acceptor units such as carboxylic acid, cyanoacrylic acid belong to $(2D-\pi-D'-A)$ architecture and $(2D-\pi-D'-A-\pi-A)$ arrangement was designed by altering anchoring group such as (E)-2-cyano-3-(5-(1cyanovinyl)thiophen-2-yl)acrylic acid.

The electrolytes also played a major role in the improvement of PCE of DSSCs via proper regeneration of dyes and suppression of recombination reactions between dye and redox couples. In conventional DSSCs mainly liquid electrolyte has been used, but it has some major drawbacks like solvent leakage and sublimation of I^-/I_3^- redox couple. This liquid electrolyte has replaced by introducing non-volatile and long-term stable polymer gel electrolyte through the incorporation of redox couple into any high conducting polymer matrix [30]. So far, among the gel polymer electrolytes the blended polymer electrolytes emerging as a stable and efficient gel electrolyte for DSSCs. These blended gel polymer electrolytes

have many advantages such as high thermal and chemical stability, better charge carrier mobility, tensile strength, flexibility, less spillage, good fluidity, excellent dielectric constant, increasing ionic conductivity and ion transfer rate [31].

In polymer electrolytes based DSSCs, many researchers promote gel polymer blended techniques that enrich performance and enhance the stability by ionic transport of dissociating ions through the blended polymer matrix. Highly admired polymers utilized so far in blended gel electrolytes are poly-(vinylidene fluoride) (PVDF), poly-acrylonitrile (PAN), poly-(ethylene oxide) PEO, polyurethane (PU), poly-(vinyl chloride) (PVC) and some other biopolymers. [32,33]. The diffusion of ions into the polymeric chain would alter the ionic conductivity of the polymer by intermolecular interaction. The blending technique helps to reduce the energy barrier of charge carrier ions, enhancement of dielectric constant, boiling point, subdues melting point and viscosity [34,35]. Typically, the blending of different polymer matrix favours the suppression of back electron transfer, increase in electron diffusion length and charge collection efficiency. [36]

Herein, we used poly-ethylene glycol (PEG) and hydroxyethyl cellulose (HEC) as polymer matrixes for blending due to their gelation behaviour, polar nature and chemically stability, superior mechanical and electrochemical behaviour. The blended (PEG-HEC) gel electrolyte influences the device performance, possesses excellent physical and chemical stability. The long-term stability issue has sorted out using a PEG-HEC blend polymer matrix with an I^{-}/I_{3}^{-} redox mediator because of its high charge mobility properties and unique photoelectrical properties. [37]

The present work addresses improvising i) The PCE of DSSCs using the well-organised structure of the indole-based small organic molecule as photo-sensitizer, ii) The stability of DSSCs by incorporating polymer matrix in the electrolyte portion. The simple and systematic procedure were designed as a (2D- π -D'-A), (2D- π -D'-A- π -A) arrangement at low cost and high yield. The proposed structures of the indole based organic dye has labelled as DPC, DTC, DPCY, DTCY, DPTCY and DTTCY respectively. These sensitizer molecules are the combination of bis-N, N'-dimethylaniline unit and indole unit as electron-donating nature and the electron relays carried through of phenyl or thienyl spacer groups as neutral groups at the para-position, lastly, the collected electron has transmitted through an identical auxiliary group possess both electronwithdrawing nature and anchoring tendency (i.e.) carboxylic acid (labelled as DTC and DPC), cyanoacrylic acid (labelled as DTCY and **DPCY**), (E)-2-cyano-3-(5-(1-cyanovinyl)thiophen-2-yl)acrylic acid) (labelled as DTTCY and DTPCY). The QSSE has prepared by blending PEG and HEC polymer with iodide redox couple and additive. The correlation study has carried on these six newly synthesized organic dyes which coupled with an I⁻/I₃⁻PEG-HEC QSSE. The photovoltaic performance, interfacial studies, electron lifetime and stability of all six dyes have determined to find a better performing organic sensitizer coupled with polymer gel electrolytes.

2. Experimental

2.1. Materials

All the required chemicals and reagents were purchased commercially and used without further purification. The organic solvents were dried with anhydrous sodium sulphate and collected under reduced pressure. The solar cell setups were purchased commercially from Solarnix, Switzerland.

2.2. Methods and instruments

The synthesized organic molecules were extracted and purified using column chromatography with silica gel (100-200 mesh)



Fig. 1. Synthetic route to synthesize organic dyes (DTC, DPC, DTCY, DPCY, DTTCY and DPTCY).

packed in thick-walled glass columns using a mixture of petroleum ether (PE) and ethyl acetate (EA) as eluent. The primary investigation on separating compound was performed by thin-layer chromatography (TLC). The eluent spot of the organic mixture was visualized using a UV chamber by the light source ($\lambda = 254$ and 365 nm). The microcontroller-based melting point apparatus was utilized for recording melting points using open capillaries. Initially, the functional group confirmations were analysed by IR-Tracer 100 FTIR spectrophotometer (ATR mode). ¹H and ¹³C NMR spectra were recorded using CDCl₃ solvent in BRUKER spectrometer at 400 MHz. The elemental composition percentage were analysed using the Elementar Vario EL III CHNS analyser used to predict carbon, hydrogen, nitrogen, and sulphur (CHNS) present in the newly synthesized compounds. The absorption spectra were obtained by the SHIMADZU UV-3600 spectrophotometer. The cyclic voltammetry (CV) and electrochemical impedance experiments were performed within an identically constructed setup connected with a Biologic SP-300 electrochemical workstation. The photovoltaic performance and incident photocurrent conversion efficiency (IPCE) was measured with Keithley 2400 source meter and a Science Tech monochromatic solar stimulator used as light source illumination of 100 mWcm² at AM-1.5G to analyze current-voltage characteristics of a testing cell.

2.3. Synthetic route of the target molecules

The structures of indole based organic molecules are shown in **Fig. 2.** We disclosed a synthetic route of designs strategy with an optimised procedure from literature. These molecules were synthesised as shown in **Fig. 1**. These procedures were purely based on the commercialisation with a simple structure, curtail the number of steps, at higher yield and usage of lowcost catalyst. The multi-step reactions have initiated from 4bromobenzaldehyde (**1a**) and 5-bromothiophene-2-carbaldehyde (**1b**) and then transformed to phosphonium salt (**3a-3b**) through primary alcohols as intermediates (**2a-2b**). Further, the phosphonium salt (**3a-3b**) were subjected to Wittig olefination with 4,4'bis(dimethylamino)thiobenzophenone using K₂CO₃ as a base to acquire cross-coupled intermediates (**4a-b**) [38]. The Ullmann coupling reaction was held between 1H-indole-3-carboxylic acid and (**4a-4b**) in presence of K_2CO_3 that yields **DPC, DTC** respectively.

To synthesis DTCY, DPCY, DTTCY, DPTCY molecules, the coupling of 1H-indole-3-carbaldehyde to (4a-4b) by Ullmann coupling to obtain the product (5a-b) respectively [39]. Moreover, the condensation 2-thiopheneacetonitrile along with 5a-b in presence of base yields 6a-b subsequently undergoes a Vilsmeier-Haack reaction to achieve desire products (7a-b). The resultant aldehyde compounds (5a-b, 7a-b) were subjected to Knoevenagel condensation using cyanoacetic acid to achieve a higher yield of final products (DTCY, DPCY, DTTCY, DPTCY). All the reactions proceeded efficiently, affording excellent yields. The intermediates and targeted molecules were purified using column chromatography and characterised. The structural characterisations of new compounds were confirmed by infrared spectroscopy, proton-1 and carbon-13 NMR techniques were shown in Figure ESI S1-S6. The elemental CHN analysis was summarised in Table S1. The detailed synthesis procedures of all the organic dyes and their intermediates were given the supporting information. The characterized results of the final dye molecules were given as follows,

1-(4-(2,2-bis(4-(dimethylamino)phenyl)vinyl)phenyl)-1Hindole-3-carboxylic acid (DPC) Brown solid (74 % yield); Mp: 138.8 - 139.8°C; R_f= 0.38 (30% EA/PE); FT-IR (ATR): 2947, 2840, 2347, 1723, 1683, 1545, 1449, 1225, 1112, 915, 774, 740, 664, 628, 527, 489 cm⁻¹: ¹H NMR (400MHz, (CDCl₃,δ in ppm): 3.07 (s,12H); 6.75 (d, 4H, J = 4 Hz); 6.91 (s, 1H); 7.24-7.35 (m, 6H,); 7.52 (d, 2H, J = 4 Hz); 7.60 (d, 2H, J = 4 Hz); 7.87 (d, 1H, J = 8 Hz); 8.40 (s, 1H); 8,95 (d, 1H, J = 4 Hz); 11.07 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, δ in ppm): 41.3, 109.5, 111.0, 111.7, 119.8, 121.8, 126.0, 126.6, 127.0, 128.7, 128.8, 129.3, 129.5, 133.4, 137.3, 137.9, 145.5, 150.3, 169.3. CHNS analysis for C₃₃H₃₁N₃O₂: C: 79.01, H: 6.23, N: 8.38. Found: C: 79.05, H: 6.17, N: 8.46.

1-(5-(2,2-bis(4-(dimethylamino)phenyl)vinyl)thiophen-2-

yl)-1H-indole-3-carboxylic acid (DTC): Bright brown solid (78% yield); Mp: 128.9 - 129.9°C; R_f = 0.42 (30 % EA/PE); FT-IR (ATR): 2768, 2755, 2389, 2195, 1703 1457, 1448, 1363, 1228, 1030, 826, 745, 673, 504 cm⁻¹; ¹H NMR (400MHz, (CDCl₃, δ in ppm): 3.07 (s,12H); 6.75 (d, 4H, J = 4 Hz); 6.91 (s, 1H); 7.20 (d, 4H, J = 4 Hz); 7.23-7.24 (m, 2H); 7.32-7.35 (m, 2H); 7.87 (d, 1H, J = 4 Hz);

2D-π–**D'**–A

2D-π–**D'**–**A-**π-**A**



Fig. 2. Molecular structures of newly synthesized organic dyes (DTC, DPC, DTCY, DPCY, DTTCY and DPTCY).

8.40 (s, 1H); 8,95 (d, 1H, J = 4 Hz); 11.07 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, δ in ppm): 41.3, 108.6, 109.5, 111.7, 113.8, 119.8, 121.8, 125.0, 126.3, 126.6, 127.1, 128.3, 128.8, 129.5, 137.8, 143.3, 144.4, 150.3, 153.6, 169.2. CHNS analysis for C₃₁H₂₉N₃O₂S: C: 73.34, H: 5.76, N: 8.28, S: 6.32. Found: C: 73.98, H: 5.90, N: 8.23, S: 6.07.

(E)-3-(1-(4-(2,2-bis(4-(dimethylamino)phenyl)vinyl) phenyl)-1H-indol-3-yl)-2-cyanoacrylic acid (DPCY) Red solid (91 % yield); Mp: 162.3 - 163.3°C; R_f= 0.36 (40 % EA/PE); FT-IR (ATR): 3098, 2886, 2211, 1719, 1652, 1590, 1412, 1247, 1146, 1152, 1025, 974, 812, 746, 688, 616, 515 cm⁻¹. ¹H NMR (400MHz, (CDCl₃, δ in ppm): 3.07 (s,12H); 6.75 (d, 4H, J = 4 Hz); 6.91 (s, 1H); 7.26 -7.29 (m, 2H); 7.34 (d, 4H, J = 4 Hz); 7.51-7.56 (m, 3H); 7.62 (d, 2H, J = 4 Hz); 7.87 (s, 1H); 8.26 (s, 1H); 8.37 (d, 1H, J = 4 Hz); 11.07 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, δ in ppm): 41.3, 92.8, 109.5, 111.7, 113.0, 117.7, 119.8, 121.8, 126.0, 126.6, 127.0, 128.7, 128.8, 129.3, 129.5, 133.4, 137.3, 137.9, 145.4, 150.3, 157.4, 159.8. CHNS analysis for C₃₆H₃₂N₄O₂: C: 78.24, H: 5.84, N: 10.14. Found: C: 78.16, H: 5.38, N: 10.39.

(E)-3-(1-(5-(2,2-bis(4-(dimethylamino)phenyl)vinyl)t

hiophen-2-yl)-1H-indol-3-yl)-2-cyanoacrylic acid (DTCY) Dark brown solid (89 % yield); Mp: 205.6 – 206.6°C; R_f = 0.36 (40% EA/PE); FT-IR (ATR): 3057, 2846, 2801, 2257, 2211, 2107, 1705, 1693, 1533, 1437, 1408, 1321, 1283, 1079, 965, 869, 732, 643, 569, 489 cm⁻¹; ¹H NMR (400MHz, (CDCl₃, δ in ppm): 3.07 (s,12H); 6.71 (d, 4H, J = 4 Hz); 6.91 (s, 1H); 7.21 (d, 4H, J = 4 Hz); 7.23 (m, 3H); 7.35 (d, 1H, J = 4 Hz); 7.52 (d, 1H, J = 8 Hz); 7.84 (s, 1H); 8.22 (s, 1H); 8.39 (d, 1H, J = 4 Hz); 11.03 (s, 1H). ¹³C NMR (100

MHz, CDCl₃, δ in ppm): 41.3, 92.8, 109.5, 110.6, 111.7, 113.8, 117.7, 19.8, 121.8, 125.0, 126.3, 126.6, 127.1, 128.3, 128.8, 129.5, 137.8, 143.3, 144.4, 150.3, 157.4, 159.8. CHNS analysis for C₃₄H₃₀N₄O₂S: C: 73.09, H: 5.41, N: 10.03, S: 5.74. Found: C: 73.14, H: 5.49, N: 10.25, S: 5.35.

E)-3-(5-((E)-2-(1-(4-(2,2-bis(4-(dimethylamino)phenyl) vinyl)phenyl)-1H-indol-3-yl)-1-cyanovinyl)thiophen-2-yl)-2cyanoacrylic acid (DPTCY) Purple red solid (81 % yield); Mp: 168.4 - 169.4°C; R_f= 0.36 (40% EA /PE); FT-IR (ATR): 2213, 1693, 1588, 1497, 1402, 1337, 1279, 1049, 950, 797, 697, 511 cm⁻¹. ¹H NMR (400MHz, (CDCl₃, δ in ppm): 3.06 (s,12H); 6.75 (d, 4H, J = 4 Hz); 6.91 (s, 1H); 7.25-7.28 (m, 2H); 7.34 (d, 4H, J = 4 Hz); 7.52-7.54 (m, 3H); 7.62 (d, 2H, J = 4 Hz); 7.78 (d, 2H, J = 4 Hz); 7.87 (s, 1H); 7.90 (s, 1H); 8,38 (d, 1H, J= 4 Hz); 8.60 (s, 1H); 11.01 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, δ in ppm): 41.3, 92.6, 109.5, 111.7, 113.0, 113.7, 117.7, 118.8, 119.8, 121.8, 126.0, 126.6, 127.0, 128.2, 128.8, 128.7, 129.3, 129.5, 130.0, 133.4, 137.3, 137.8, 141.3, 143.2, 145.3, 150.3, 153.5, 159.8. CHNS analysis for C₄₃H₃₅N₅O₂S: C: 75.30, H: 5.14, N: 10.21, S: 4.68. Found: C: 75.02, H: 5.26, N: 10.83, S: 4.21.

(E)-3-(5-((E)-2-(1-(5-(2,2-bis(4-(dimethylamino)phenyl) vinyl)thiophen-2-yl)-1H-indol-3-yl)-1-cyanovinyl)thiophen-2-yl)-2-cyanoacrylic acid (DTTCY) Dark red solid (84 % yield); Mp: 186.8 - 187.8°C; R_f = 0.39 (40 % EA/ PE); FT-IR (ATR): 3031, 2931, 2845, 2219, 1707, 1695, 1564, 1446, 1409, 1341, 1262, 1175, 1011, 937, 811, 752, 697, 626, 517, 469 cm⁻¹.¹H NMR (400MHz, (CDCl₃, δ in ppm): 3.07 (s,12H); 6.71 (d, 4H, J = 4 Hz); 6.91 (s, 1H); 7.20 (d,



Fig. 3. Absorption spectra of DTC, DPC, DTCY, DPCY, DTTCY and DPTCY dye recorded a) in CHCl₃ (0.04 mM) b) after absorption on TiO₂ surface.

4H, J = 4 Hz); 7.23-7.24 (m, 3H); 7.33 (d, 1H, J = 4 Hz); 7.52 (d, 1H, J = 4 Hz); 7.74 (d, 2H, J = 4 Hz); 7.84 (s, 1H); 7.91 (s, 1H); 8.39 (d, 1H, J = 4 Hz); 8.64 (s, 1H); 11.01 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, δ in ppm): 41.3, 92.6, 109.5, 110.6, 111.7, 113.5, 113.8, 117.7, 118.5, 119.8, 121.8, 125.0, 126.3, 126.6, 127.1, 128.3, 128.4, 128.8, 129.5, 129.9, 137.8, 141.3, 142.3, 143.3, 144.4, 150.3, 153.3, 153.6, 159.8. CHNS analysis for C₄₁H₃₃N₅O₂S₂: C: 71.18, H: 4.81, N: 10.12, S: 9.27. Found: C: 71.03, H: 4.76, N: 10.21, S: 9.50.

2.4. Preparation of QSSE

Initially, the liquid electrolyte was prepared via mixing of 0.1 M of potassium iodide and 0.05 M of iodine, 0.6 M 1-methyl-3propyl imidazolium iodide as an ionic solvent and 0.5 M 4-tertbutylpyridine as an additive under ambient temperature. Subsequently, the gel polymer electrolyte was prepared by in-situ blending of (PEG-HEC) matrix (total 0.3g in 1:1 ratio) in dimethylformamide with the prepared liquid electrolyte and further stirred at 60-70°C until homogenous mixture formation. The gelation of the QSSE image is shown in **Fig. 5a**

2.5. Device fabrication

The solar cell setup was commercially purchased from Solaronix in Switzerland, consist of TiO₂ coated transparent FTO glasses plates $(2.0 \times 2.0 \text{ cm}^2)$ with an active surface area of 0.36 cm² as a photo-anode and a platinum-coated FTO plate as a counter electrode. The photo-anode (active area $0.6 \times 0.6 \text{ cm}^2$) was immersed into 0.5 mM (DTC, DPC, DTCY, DPCY, DTTCY and DPTCY) solution in ethanol for 24h at room temperature. After complete adsorption of sensitizers on the anode surface, the electrodes were rinsed with ethanol and dried. The platinum-coated FTO glass plate was sandwiched by surlyn film as a spacer with alligator clips. The cell setup was completed by filling the electrolyte in between two electrodes. A black mask with a suitable aperture was used on the devices during the photovoltaic analyses.

3. Results and discussions

3.1. Photo-physical properties of sensitizer molecules

The light absorption ability of DTC, DPC, DTCY, DPCY, DTTCY and DPTCY sensitizer were investigated using UV-visible absorption spectra. A linear intense absorption spectrum was recorded using an aprotic solvent. These organic molecules are record in C=4.0 $\times 10^{-5}$ M chloroform solutions displays in Fig. 3a and resultant parameters were tabulate in Table 1. A stretched band in

the high energy region 340 to 400 nm, attributes in π - π * electronic transitions of the conjugated molecule as a backbone. A broad peak in low energy region 400 to 500 nm attribute due to intramolecular charge transfer (ICT) and delocalisation of the molecule. The absorption maximum (λ_{max}) of dye can be finetuned by replacing π -conjugation relay. While increasing the withdrawing group on the dye molecules, a wide absorption spectrum was attained in the UV-Visible light region. A redshift occurs for both the dyes DPTCY and DTTCY due to their delocalisation and better light-harvesting properties. [40]. The electronic transition between HOMO and LUMO energy level was determined as bandgap (E_g^{opt}) using the λ_{onset} value of the optical absorption band

$$E_g^{opt}$$
 $(eV) = \frac{1240}{\lambda_{onset}}$

According to Lambert-Beer law, the molar extinction coefficients (ε) of these sensitizers were calculated and tabulated in **Table 1.** These organic sensitizer exhibits (ε) in the range of 28,000 to 45,000 M^{-1} cm⁻¹ comparably higher than ruthenium complex dye N3 and N719 dyes [41]. The analysis of molar absorptivity values reveals that DTTCY dye possesses the highest ε (45177 M⁻¹cm⁻¹) among the series of dyes, due to its elongation π -conjugation system. Moreover, the optical property of the sensitizer had investigated after absorbing on the TiO₂ surface and the plot was shown in Fig. 3b. They exhibited a wide ICT band with a redshift in absorbance maxima on the TiO₂ surface, which attributes to J-aggregation [42]. It occurs due to aromatic π - π stacking and orient within molecules like head to tail fashion. The strong interactions held between anchoring moieties of the molecule and TiO₂ surface owing to the deprotonation of the acid group and supports in the electron displacement and improves the performance of DSSCs. An increase in the count of the electron-withdrawing group (cyano) results in a powerful red-shift in absorption edges (λ_{onset}) around 544 and 666 nm. The energy bandgap (E_g^{opt}) of these indole based dye molecules were acquired between 2.28 and 1.86 eV respectively. These synthesised dyes show a broad absorption window towards the near IR region, efficient electron injection capability and thus beneficial in attaining higher Voc and PCE for DSSCs.

3.2. Electrochemical studies of sensitizer molecules

The cyclic voltammetry studies have performed to determine the HOMO and LUMO energy levels of newly synthesized organic dye. The energy levels of dyes were analyzed to find redox potential suitability towards the TiO_2 and electrolyte. A total of

Table 1

Photo-physical and Electrochemical parameters of new synthesized DTC, DPC, DPCY, DTCY, DPTCY and DTTCY molecule.

	Photo-physical properties				Electrochemical properties		
Sensitizer	· λ _{max} ª/nm	ε^{a} /M ⁻¹ cm ⁻¹	$\lambda_{max}/\lambda_{onset}^{D}/nm$	Eg ^{opt} /eV ^c	E^{0x_1}/V^{α}	E _{HOMO} /eV ^e	E _{LUMO} /eV ^r
DTC	408	28347	443/556	2.23	1.09	-5.48	-3.25
DPC	383	28482	423/544	2.28	1.05	-5.44	-3.16
DTCY	433	35605	488/623	1.99	0.90	-5.29	-3.30
DPCY	430	33365	477/608	2.04	0.89	-5.28	-3.24
DTTCY	495	45177	539/666	1.86	0.84	-5.23	-3.37
DPTCY	482	43942	515/650	1.91	0.83	-5.22	-3.31

^a Absorption maximum wavelength and molar extinction coefficient of dye molecules measured in CHCl₃ solution.

 $^{\rm b}$ Absorption maximum wavelength of dye molecules sensitized on ${\rm TiO}_2$ surface.

^c Bandgap was determined from λ_{onset} using, E_g^{opt} /eV = 1240/ λ_{onset} .

^d *E*^{ox1} is the first oxidation potentials respectively compounds;

^e E_{HOMO} was calculated using the formula, $E_{\text{HOMO}} = -[(E^{\text{ox1}} - E_{1/2(\text{ferrocene})}) + 4.8]$ eV, given that $E_{1/2(\text{ferrocene})} = 0.41$ V;

^f Since the reduction process was not observed clearly, E_{LUMO} was calculated by $E_{LUMO} = E_{HMO} + E_g^{opt}$;



Fig. 4. a) Cyclic voltammogram for synthesized organic dyes at a scan rate of 50 mV s⁻¹. b) Energy level diagrams of synthesised organic molecules.

2.0 × 10⁻³ M solution of organic molecules in acetonitrile was drop-cast onto a glassy carbon electrode surface which acts as a working electrode. The platinum wire and silver wire was served as a counter electrode and reference electrode respectively. The measurements were performed using 0.1 M *n*Bu₄ClO₄ supporting electrolyte at a scan rate of 50 mV s⁻¹. The calibration was done using a standard ferrocene/ferrocenium as the redox couple show in **Figure ESI S7**. We obtain $E_{1/2(\text{ferrocene})}$ value of ferrocene as 0.48 V. The HOMO energy levels of all compounds were derived from the first oxidation potential (E^{ox1}) using the following Pommerehne empirical relation [43,44].

$E_{HOMO} = -\left| \left(E^{ox1} - E_{1/2(ferrocene)} \right) + 4.8 \right| eV$

The first oxidation potential of organic dyes falls in the order, **DTC** (1.09 V) < **DPC** (1.05 V) < **DTCY** (0.90 V) < **DPCY** (0.89 V) < **DTTCY** (0.84 V) < **DPTCY** (0.83 V) were shown in **Fig. 4a**. These results prove that π -conjugation spacer of phenyl containing dyes DPC, DPCY and DPTCY showed low oxidation potentials than the thienyl dyes DTC, DTCY and DTTCY. The shift in the oxidation peak of organic dyes is due to their acceptor units. The lower oxidation potentials acquired for **DPTCY** and **DTTCY** molecules because of their electron-withdrawing capability of (E)-2-cyano-3-(5-(1-cyanovinyl)thiophen-2-yl)acrylic acid. The HOMO energy level of DTC, DPC, DTCY, DPCY, DTTCY and DPTCY compounds were calculated from the above equation. Their resultant E_{HOMO} values are -5.48, -5.44, -5.29, -5.28, -5.23, and -5.22 eV respectively. The low-lying HOMO energy levels of these indole based organic molecules are lesser than the potential level of I^-/I_3^- an electrolyte that responsible for efficient the regeneration process of the dye molecules. The electron transfer from LUMO of indole based organic molecules should be higher than the conduction band of TiO₂ which permits the efficient photo-generated electron injection and suppress the back-electron transfer [45]. These results provide a way to enhance the PCE of DSSCs [46,47]. Since these molecules exhibit quasi-reversible behaviour, the cathodic process was forbidden, and the LUMO energy levels were obtained by the following formula [48].

$$E_{LUMO} = E_{HOMO} + E_g^{opt}$$

The calculated LUMO energy levels from the above equations are -3.25, -3.16, -3.30, -3.24, -3.36 and -3.32 eV corresponds to E_{HOMO} and $E_{\text{g}}^{\text{opt}}$ tabulated in **Table 1**. The energy level diagram of the dyes was represented in **Fig. 4b.** The optical band-gap of this indole based sensitizer lies in the range of 2.28 to 1.86 eV where their HOMO energy level varied from - 5.48 to -5.22 eV, results in a gradual increment in photo-current. The sub-electronic energy levels of dye molecules have altered due to the change in the acceptor unit, π -configuration group. There is a trivial change in the replacement of the phenyl to thienyl group spacer because of electron delocalisation. The change in acceptor nature had possessed a remarkable improvement in the HOMO-LUMO energy level which is quite useful in the enhancement of PCE. [49]



Fig. 5. a) Photographic image, b) Absorption spectra, c) DSC Thermogram, d) FESEM image and EDAX characteristics, e) XRD spectra of Quasi-solid state gel electrolyte.

3.3. Properties of QSSE

We introduced a new blending gel polymer electrolyte (GPE) to improve the stability and PCE of organic dye-based DSSCs. Herein, biopolymer HEC was blended with PEG to form a stable iodine redox-based QSSE. The presence of polyethylene glycol in electrolyte facilitates the crosslinking with HEC to form polymer gel, whereas the presence of redox couple produces a polymer iodine complex. This will contribute to enhancing the conductivity and photovoltaic performance of prepared PEG-HEC QSSE. The ionic conductivity values for GPE are lower than those for the liquid electrolyte, due to the lower crystallinity that limits the mobility of I_2 in the polymer matrix. However, I^-/I_3^- ion release from the polymer iodine complex and can easily accomplish greater efficiency. The conductivity of PEG-HEC QSSE as 1.55×10^{-3} S cm⁻¹ depends on their amorphous nature, structural morphology and it may respond to the photovoltaic performance of the device. The PEG-HEC QSSE. has subjected to further reliable investigation.

3.3.1. Photo-physical properties

A comparison of absorption spectra between Liquid electrolyte (LE), Gel polymer electrolyte (GPE) and PEG-HEC gel polymer has presented in **Fig. 5b**. The blank polymer contains no intense absorption peak. On other hand, we have observed a difference in intensity between LE and GPE confirms the attachment of iodolyte into the polymer matrix. An intense peak appeared at 208 nm 292 ($\sigma \rightarrow \sigma^*$) and 363 nm ($\pi \rightarrow \sigma^*$) belongs to I₃⁻ ion of the gel electrolyte. The in-situ reaction held within the GPE and iodine species enriches the redox behaviour of electrolyte that avoids sublimation of the iodine ions.

3.3.2. DSC and XRD

The crystallinity of blended polymer gel electrolyte has characterised using differential scanning calorimetry (DSC). As on literature, HEC polymer reports the glass transition temperature (T_g) at 120-127°C, crystallization temperature (T_c) peaks at approximately 240°C and the melting temperature (T_{m}) at 308°C. From DSC thermographs displayed in Fig. 5c, for PEG-HEC QSSE, the phase transition T_g at 70°C can be identified and this lower T_g was responsible to attain a suitable electrolyte material. The endothermic peak was considered as its crystallisation temperature T_c at 167°C, this possesses free mobility of ions. The exothermic peak was determined as melting temperature T_m at 370 °C. These results satisfy the lower crystallinity behaviour of GPE and therefore it supports better charge mobility and conductivity. The amorphous nature of GPE has confirmed by XRD conducted at a scanning rate of 5°/min over a 2h interval from 10 to 80 degree. In Fig. 5e, PEG-HEC blended composite has diffraction peaks at 25.9 degrees. From our observation, the characteristic peaks were amorphous for GPE and this property may lead to having a higher ionic conductivity.

3.3.3. Morphology

The morphology of the prepared PEG-HEC QSSE was studied using a Field emission scanning electron microscope. From **Fig. 5d**, we observed that different surface morphologies for bare PEG-HEC polymer and I^-/I_3^- /PEG-HEC based polymer gel electrolyte respectively. The observed change was primarily due to crosslinking between the polymer gel and the iodine complex. The uniformity of dispersed cubic crystal formation on the surface of PEG-HEC based polymer gel electrolyte imparts improved electrical conductivity to the electrolyte. The distribution of elements into the prepared gel polymer matrix has characterized using EDAX. The spectrum shows the wt% values of elements which are shown in Table and it also confirms the gelation of the polymer electrolyte. [50]



Fig. 6. a) Rrec and Rpt Values b) lonic Conductivity and Dapp Values c) Nyquist plots d) Bode phase angle plots for organic dyes/I-/I₃-/PEG-HEC.

3.4. Ionic conductivity

The ionic conductivity of devices with prepared DTC, DPC, DTCY, DPCY, DTTCY and DPTCY dyes coupled with PEG-HEC QSSE was calculated from the following formulae, [51]

$$\sigma = \frac{I}{R_b A}$$

Where I, is the distance between the two electrodes, A is the active surface area of the fabricated device R_b is the bulk resistance obtained from the impedance curve. The ionic conductivity has calculated and tabulated in **Table 3** and shown in Fig. 6a. The ionic conductivity of GPE was varied from 1.23×10^{-3} to 1.13×10^{-3} , upon the influence of organic dye used. The interaction between organic dyes $/I^{-}/I_{3}^{-}/$ PEG-HEC QSSE was healthier due to a larger ion transport inside the polymer chains of the gel electrolytes. These results prove that PEG-HEC blended gel state electrolyte leads a vital role to maintain the conductivity of organic dyes-based devices.

3.5. Electrochemical impedance spectroscopy studies

The EIS studies for DSSC devices consist of organic dyes coupled with PEG-HEC blended gel electrolyte were carried out under AC amplitude of 10 mV in the frequency range of 10^2 - 10^6 Hz at their open-circuit conditions. The resultant Nyquist plot consists of two semicircles corresponds to (R_{Pt}) and (R_{rec}). The charge transfer resistance (R_{pt}) is the resistance between the (Pt) counter electrode/electrolyte interfaces. The resistance occurs during recombination TiO₂ adsorbed dye molecules/electrolyte interfaces as charge recombination resistance (R_{rec}). R_s referred to as the series resistance. The chemical capacitance between photo-anode and

Table 2 Electrochemical Impedance Spectroscopy data of DTC, DPC, DPCY, DTCY, DPTCY and DTTCY organic photo-sensitizer with PEG-HEC polymer gel electrolytes.

Devices	R _s /ohm	R _{rec} /ohm	R _{pt} /ohm	$C_{\mu}/\mu F$
DTC/I ⁻ /I ₃ ⁻ /PEG-HEC	22.78	14.32	2.09	7.61
DPC/I ⁻ /I ₃ ⁻ /PEG-HEC	24.35	10.95	2.01	6.29
DTCY/I ⁻ /I ₃ ⁻ /PEG-HEC	22.74	26.33	2.33	11.84
DPCY/I ⁻ /I ₃ ⁻ /PEG-HEC	22.57	17.73	2.23	8.15
DTTCY/I ⁻ /I ₃ ⁻ /PEG-HEC	24.62	53.97	2.46	17.02
DPTCY/I ⁻ /I ₃ ⁻ /PEG-HEC	24.13	49.22	2.35	13.63

electrolyte referred to as (C_{μ}). The obtained Nyquist plots were fitted with an equivalent circuit as shown in the inset of **Fig. 6c** using Z-fit software and tabulated in **Table 2**. The lower R_{Pt} resistance values about (2.01-2.46 ohm) for organic dyes/ $I^{-}/I_{3^{-}}$ / PEG-HEC QSSE implies that there is a lower resistance at Pt/electrolyte interfaces which favours larger I⁻ ions formation in the devices. On other hand, especially the four organic dyes contain cyanoacetic acid as an anchor group coupled with PEG-HEC QSSE attained the higher R_{rec} about (17.73-53.97 ohm) and C_{μ} about (8.15-17.02 μ F) which attributes suppression in recombination reactions between TiO₂ and I_3^- ion of the devices. These EIS results satisfy that combination of novel Indole based organic dyes possess a strong acceptor group was the blended efficiently and reduce the recombination processes of devices for larger V_{OC} and better stability.

3.6. Electron lifetime and diffusion coefficient

The recombination phenomenon between the novel indole based organic dyes/ I^-/I_3^- / PEG-HEC QSSE can be understood from the electron lifetime (τ) which was calculated using Bode phase

Table 3

lonic conductivity, Diffusion co-efficient and electron lifetime data of DTC, DPC, DPCY, DTCY, DPTCY and DTTCY organic photo-sensitizer with PEG-HEC polymer gel electrolytes.

Devices	σ (10 ⁻³)/S cm ⁻¹	Dapp $(10^{-7})/cm^2 s^{-1}$	$\mathrm{f}_{\mathrm{max}}/\mathrm{Hz}$	τ_n/ms
DTC/I ⁻ /I ₃ ⁻ /PEG-HEC	1.22	1.25	2.976	53.46
DPC/I ⁻ /I ₃ ⁻ /PEG-HEC	1.14	1.10	3.161	50.33
DTCY/I ⁻ /I ₃ ⁻ /PEG-HEC	1.22	3.20	2.838	5606
DPCY/I ⁻ /I ₃ ⁻ /PEG-HEC	1.23	2.35	2.940	54.11
DTTCY/I ⁻ /I ₃ ⁻ /PEG-HEC	1.13	4.25	2.719	58.51
DPTCY/I ⁻ /I ₃ ⁻ /PEG-HEC	1.15	3.51	2.778	57.27

plot Fig. 6d from the following equation [52],

$$\tau_n = \frac{1}{2\pi f_{max}}.$$

The f_{max} is the maximum phase-frequency in the low-frequency region. The electron lifetime of the new organic sensitizer was differing from each other due to the properties of internal standard and blending of PEG-HEC QSSE. The lifetime results were shown in Table 2 and it reveals the order of electron lifetime is decreasing as DTTCY > DPTCY > DTCY > DTC > DPC. The shorter τ value observed for DPC/I⁻/I₃⁻/ PEG-HEC QSSE indicates a low charge recombination potential between TiO₂/electrolyte interfaces, whereas DTTCY/I-/I3- PEG-HEC QSSE observed longer au value readily lowers recombination rate and reliable in antiaggregation on the anode surface that improves the Voc. It can be understood from the lifetime results that the combination of indole based organic dyes with PEG-HEC QSSE enhances the efficiency as well as stability owing to the lower recombination process of the devices [53]. Moreover, the combination of new organic dye materials with PEG-HEC QSSE increases the electron lifetime of the device increases leads to the improvement in Jsc and Voc, which yields significantly enhanced PCE.

The diffusion of I_3^- ion into organic DTC, DPC, DTCY, DPCY, DTTCY and DPTCY dyes towards the platinum electrode has an important role for DSSCs device. Thus, the D_{app} (apparent diffusion coefficient of Tri-iodide) parameter was listed in **Table 3**. The enhancements of PCE in DSSC are mainly for the QSSE. The calculated D_{app} values for organic dyes/ I^-/I_3^- / PEG-HEC QSSE using the following equation, [54]

$$D_{I_3^-} = \frac{i_{lim} L}{2nFC_0}$$

Where, n- Number of electron transfer from redox pair (n=2), F-faraday's constant, L-Distance between two electrodes (L=100µm), C₀-Molar concentration of I_3^- (C₀=0.05 M) the diffusion limiting current density has determined from cyclic voltammetry at scan rate 5mVs⁻¹. The diffusion coefficient of QSSE has varied due to the incorporation of I_3^- ions into polymer matric that increases I^- ion concentration that results in increasing the J_{sc} of DSSCs

3.7. Photovoltaic performance

The photovoltaic performance (photocurrent-voltage (I-V) characteristics) of fabricated DSSCs device using N3, DTC, DPC, DTCY, DPCY, DTTCY and DPTCY as dyes with PEG-HEC based polymer gel electrolyte has investigated under-stimulated light condition (AM 1.5G illumination of 100 mW cm⁻²) and demonstrated in **Fig. 7a**. The PCE of solar energy to electrical energy has calculated from short circuit current density J_{sc} , open circuit photo-voltage V_{oc} , Fill factor FF, and the incident photon flux (P_{in}) was 100 mW cm⁻². The corresponding photovoltaic parameters have summarized in **Table 4**. The J_{SC} was directly proportional to the electron collection efficiency from electrodes, V_{oc} was the potential difference between the fermi levels of dye molecules and redox potential of the redox couple, FF was maximum power related to the total resistance of DSSCs. The overall light to electricity conversion efficiency performance has estimated by the following equation,

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}}$$

The overall PCE of a photo-electrochemical cell fabricated with organic dyes and PEG-HEC QSSCs lies in the range of 1.22- 6.24%. The ruthenium N3 dye has also fabricated under the same experimental condition, it shows a better efficiency compared to our synthesised organic dye due to less charge recombination between the injected electron in the photoanode and the electrolyte. The improvement in Voc depends on the structures of dyes, which that the spacer carrying phenyl unit (DPCY, DPTCY) superior to the thienyl unit contained dyes (DTCY, DTTCY) respectively. This is mainly due to the low resonance energy of thienyl units compared to phenyl unit carrying dye that results in a lower charge recombination rate. However, DSSCs device fabricated with sensitizer having carboxylic acid as anchoring core DTC & DPC attained PCE of 1.88 and 1.22 % which was lower while compared to sensitizer having cyanoacetic acid as anchoring core DTCY & DPCY showed PCE of 4.86 % and 3.72 % respectively. These results may occur due to the presence of cyano moiety in the acceptor end, shows a strong ICT absorption band and harvest higher Jsc. Herein, sensitizer DTTCY & DPCY obtained higher PCE of 6.24 % and 5.92 % due to the presence of strong electron-withdrawing moieties results in the redshift of absorption spectra compared with DTCY, DPCY sensitiser. These PCE enhancements were also due to increasing the count of cyano moiety in the acceptor part of sensitizer readily enrich electron delocalization between donor and acceptor ends. The trend set observed in photon to the current conversion efficiency of the synthesised indole based organic dyes with PEG-HEC QSSCs electrolyte were in the order DTTCY > DPTCY > DTCY > DPCY > DTC > DPC. The difference shown in PCE with variation in the anchoring group was due to the binding abilities and charge transport of synthesised dye on the TiO₂ surface. The overall performances of organic dye may occur due to the light-harvesting capacity of dye and efficient electron injection. The ionic conductivity and diffusion coefficient values were reliable and justice in improved Jsc values. The PEG-HEC QSSE associated with good gelation and proper pores filling on the porous TiO₂ layer, resulting in better interfacial contact between the gel polymer electrolyte and photoanode surface. The PEG-HEC QSSE helps in decreasing the concentration of I_3^- ion that suppresses the reaction with injected electron to improve the Voc value of the device.

3.8. IPCE

The incident photon to current conversion efficiency (IPCE) is a function of particular wavelengths which has studied for obtaining the light-harvesting property and also analyzes external quantum efficiency (EQE). The absorption band of organic dyes/ $I^-/I_3^-/$ PEG-HEC QSSE have absorbed in a wider range in the visible region about 600 nm which records a good photocurrent shown



Fig. 7. a) Photo voltaic studies and b) IPCE spectra of sensitized dyes performance for organic dyes/I⁻/I₃⁻/PEG-HEC.

 Table 4

 Photovoltaic performance of device by DTC, DPC, DPCY, DTCY, DPTCY and DTTCY organic photo-sensitizer with PEG-HEC polymer gel electrolytes.

Devices	V _{oc} /V	$J_{sc}/mA\ cm^{-2}$	FF /%	η /%	IPCE/%
DTC/I ⁻ /I ₃ ⁻ /PEG-HEC	0.66 ± 0.008	4.82 ± 0.14	58.84 ± 0.95	1.88 ± 0.05	14.33
DPC/I ⁻ /I ₃ ⁻ /PEG-HEC	0.52 ± 0.002	4.26 ± 0.15	55.56 ± 0.18	1.22 ± 0.05	24.01
DTCY/I ⁻ /I ₃ ⁻ /PEG-HEC	0.68 ± 0.010	12.37 ± 0.10	59.19 ± 0.63	4.86 ± 0.03	23.54
DPCY/I ⁻ /I ₃ ⁻ /PEG-HEC	0.78 ± 0.007	9.08 ± 0.16	53.40 ± 0.36	3.72 ± 0.01	26.34
DTTCY/I ⁻ /I ₃ ⁻ /PEG-HEC	0.69 ± 0.006	16.39 ± 0.21	55.5 ± 1.14	6.24 ± 0.06	39.84
DPTCY/I ⁻ /I ₃ ⁻ /PEG-HEC	0.75 ± 0.001	13.56 ± 0.11	58.02 ± 0.93	5.92 ± 0.05	32.05
N3/I ⁻ /I ₃ ⁻ /PEG-HEC	0.81 ± 0.001	17.73 ± 0.51	56.03 ± 0.23	8.08 ± 0.05	-

The Average values of three different devices, with the corresponding standard deviations. Active area: 0.36 cm², photo-anode thickness 5 mm.

in **Fig. 7b.** The QSSE showed the maximum EQE for DTTCY sensitizer of 39.84% around 400 nm while others are comparatively less. EQE of these organic dyes are ordered as follow DPC < DTC < DPCY < DTCY < DPTCY < DYTCY. The sensitizer with higher IPCE has maximum light-harvesting properties of DSSCs. The sensitizer DPTCY & DPCY shows higher V_{OC} may due to the presences of non-planar π -conjugation linkers that reduce the dark current, improvise light-harvesting and quenched the back-electron transfer. The lengthening of linear structure in DTTCY & DPTCY dye may form a dense layer on the TiO₂ surface in the presence of a strong electron-withdrawing unit. Therefore (2D- π -D'-A- π -A) arrangement has designed to protect electrolyte penetration on photo-anode TiO₂ and hold back charge recombination.

3.9. Photo-stability test

The stability assessment for a fabricated device with organic dyes/ $I^-/I_3^-/$ PEG-HEC QSSE maintained over a period of 120 h under irradiation of 1 sun illumination. The continuous illumination of light process on the fabricated cell to estimate J_{sc} , V_{oc} , FF, and η values in an interval period at room temperature are correlated in Fig. 8. The cell setup was quantified using the three devices repeatedly. Initially, the J_{sc} of the dyes is relatively constant, while V_{oc} are almost unchanged and FF was floated. After some time photo-voltage got dropped may due break in the covalent linkage of dye units [55]. As a result, the PCE maintained 90% of the initial level after 120 h under light condition respectively.

The nature of the polymer matrix and in-situ blend protects iodine sublimation, harvest maximum conductivity and resist the direct contact of the electrode. Effective progress has noticed while using polymer matrix onto the DSSCs device setup. The polymer blend with a multi-component matrix may have a small drop in conductivity but results in enhance viscosity which improves the stability of the devices. The V_{oc} of this setup has stabilised by protecting the photo corrosion of dye molecules compared to LE. The corrosive obtained on the counter electrode have reduced and these synergistic effects inspire to focus more on the development of stable QSSE DSSCs.

4. Conclusion

In summary, the indole-based organic dyes having a low lying bandgap (1.86-2.28 eV) with favourable HOMO (-5.22 to -5.48 eV) and LUMO (-3.16 to -3.36 eV) energy levels make them suitable candidates for metal-free organic dye materials in QSS-DSSCs. A correlation study carried on differently structured organic dyes coupled with a PEG-HEC blended QSSE, to analyse the vital importance of dyes and electrolytes in DSSCs. Among the six organic dyes, the DTTCY/I⁻/I₃⁻/PEG-HEC shows an effective charge separation associated with the charge transfer absorption influenced in better photovoltaic performance PCE (η) of 6.24 % with J_{sc} of 16.39 mA cm⁻², V_{oc} of 0.697 V, FF of 55.5%. The PCE improvement was mainly due to the high binding absorption of the anchoring group on TiO₂ and also the influence of QSSE which reduces recombination reaction. The influence of indole based organic dyes with PEG-HEC QSSE was elaborately understood through interfacial charge transfer kinetics (EIS), lifetime and diffusion coefficient studies of the devices. The stability of the fabricated devices was excellent under continuous 1 sun illumination radiation due to the nature of electrolyte species. This research opens a way to replacement of costly metal complex dyes and liquid electrolytes in the DSSCs world by introducing devices comprised of low-cost novel indole based derivative sensitizers with PEG-HEC QSSE.



Fig. 8. Photo-stability test for organic dyes/I-/I₃-/PEG-HEC.

Author statement

The manuscript entitled "Novel Indole-Based Photosensitizers Coupled with PEG-HEC Quasi-Solid-State Electrolyte to Improve Energy Conversion and Stability of Organic Dyes Based-Dye Sensitized Solar Cells" is new work in dye-sensitized solar cells field. There are no potential conflicts of interest and hereby declare that this article has been neither copyrighted, classified, published, nor is being considered for publication elsewhere.

Declaration of Competing Interest

There are no conflicts to declare.

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Supplementary materials

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