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Effect of mono- and di-anchoring dyes based on o,m-difluoro substituted phenylene spacer in liquid and solid state dye sensitized solar cells

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ABSTRACT

Novel mono- and di-anchoring organic dyes have been designed and synthesized with *o*,*m*-difluoro substituted phenylene spacer and were tested for DSSCs in presence of solid-state (SJE-4) as well as liquid (BMII) electrolytes. The new and simple structures of **Cz-D1** and **Cz-D2** dyes have same carbazole donor unit with either one or two side substitution of *o*,*m*-difluoro substituted phenylene π -spacer and cyanoacrylic acid acceptor. The photophysical and electrochemical properties of photosensitizes are investigated in detail and correlated with the solar cell performance. The **Cz-D2** dye have ~20% higher device efficiency than **Cz-D1** due to its lower LUMO level, and presence of two acceptor groups which provide efficient electron extraction from carbazole donor, lesser aggregation, high molar extinction coefficient and better charge transfer. Without using any additive, **Cz-D2** exhibited an attractive power conversion efficiency (PCE) of 5.35% (*Jsc* = 10.38 mA/cm², Voc = 0.75 V and FF = 0.60) in presence of iodide redox electrolyte. These dyes exhibit comparatively less efficiency when used to fabricate a solid state dye sensitized solar cell in presence of SJE-4 electrolyte due to aggregation between fluorine substituted phenylene spacer and electrolyte through strong H-bonding that might cause more electron recombination/back electron transfer. Good stability was also observed for both the dyes.

1. Introduction

To resolve the energy crisis and global environment issues alternate renewable energy sources are required to be developed [1–3]. Dye-sensitized solar cells (DSSCs) are an attractive alternative to conventional solar cell, because of their reasonable solar to electricity conversion efficiency. Due to the high production cost of silicon solar cells, scientists are focusing on organic-materials based solar cells to replace the traditional inorganic semiconductor technologies [4–23]. Since its discovery in 1991, DSSC is fast growing technology because of low material cost, low production cost, facile fabrication process, reasonable power conversion efficiency (PCE) and less environmental issues [4,5,8–20]. Typically, DSSC is an electrochemical cell consisting of a transparent conductive glass sheet (ITO/FTO) coated with a thin film of mesoporous nano-crystalline TiO₂ as an anode and monolayer of dye molecules being used as a sensitizer, capped with a counter electrode and filled with electrolyte system in between the electrodes [8–20]. Extensive efforts to improve every component of DSSC to achieve higher PCE have been made over the years. To date, highest PCE of >10% has been achieved with porphyrin and Ru based dyes in presence of liquid/solid electrolyte [9–13]. However, for the large scale application, these dyes are not favorable because of the high cost of "Ru" metal, tedious separation process, low molar-extinction coefficients and environmental issues [22]. Recently, scientists have paid attention on metal-free organic dyes due to their low cost, simple preparation, easy purification, high molar-extinction coefficients and environmental friendliness. The advantage of structural diversity in metal-free organic dyes allows us to easily tune optical and electrochemical properties. Although a decent PCE of \sim 14% has been achieved with metal-free dyes [24], investigation of novel organic dyes is still challenging and

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desirable to overcome the energy crisis.

The PCE and stability of a DSSC can be enhanced by controlling the light harvesting, charge recombination, dye regeneration, and electron injection properties of the dye [25] and these factors are strongly associated with the dye structure. Planar units with large conjugation were utilized in the dye structure to improve its light harvesting ability and achieve high absorption [26,27]. Charge recombination with the electrolyte was curtailed by incorporating bulky group or alkyl chains on the dye molecule which prevents the direct contact of electrolyte with the TiO₂ surface [28]. Co-adsorbents such as deoxycholic acid (DCA) and chenodeoxycholic acid (CDCA) are being used as anti-aggregation agents to suppress dye aggregation over the surface of TiO₂ [29,30]. Considering these points, new metal-free organic sensitizers can be designed to achieve high efficiency and stability in DSSCs.

Herein, two new o,m-di fluoro substituted phenylene spacer dyes with mono- and di-anchoring groups have been synthesized. The new and simple structure of Cz-D1 and Cz-D2 dyes have same carbazole donor unit, o,m-difluoro substituted phenylene π -spacer and cyanoacrylic acid (CAA) as acceptor, and only variation is presence of monoand di-anchors, respectively (Fig. 1). Fluorine (F) atom was incorporated into π -bridge due to its capability to tunes the molecular energy levels (lowering the LUMO level), and improve the electron mobility [7, 15-17]. Linear octyl chain on carbazole moiety was used for the better suppression of dye aggregation on metal oxide surface (TiO₂). It is clear from our previous reports that carbazole is the best donor in simple D- π -A dyes with ortho/meta-F substituted phenylene spacer [22,23]. The planarity of backbone in carbazole based dyes improves charge transfer from donor(D) to acceptor(A), results in high molar extension coefficients (ε) and long life time values. The molecular properties of the newly synthesized dyes were extensively studied and correlated with the photovoltaic performance for both liquid as well as solid state DSSCs (ss-DSSCs). Further, electrochemical impedance spectroscopy (EIS) measurements were used to estimate carrier transport and interfacial charge recombination in the solar cell devices.

2. Results and discussion

2.1. Optical characterization

Fig. 2 displays the photophysical properties of **Cz-D1** and **Cz-D2** dyes in chloroform solution as well as on TiO₂ film and the corresponding characteristic data are summarized in Table 1. Both the dyes exhibited two strong distinct absorption bands in CHCl₃ solution in the range of 200–350 nm. These peaks correspond to the localized aromatic π - π * transitions of conjugated back bone. **Cz-D1** exhibited a weak absorption band in the range of 350–500 nm which is related to the intramolecular charge transfer (ICT) from D to A. Compare to **Cz-D1**, di-anchor dye **Cz-D2** exhibited strong ICT peak as both acceptor units help in efficient electron extraction from carbazole donor and reduces H-aggregation in solution and solid state. **Cz-D1** has strong aggregation in CHCl₃ and TiO₂ surface due to the close packing, generally observed in mono-anchoring dyes. **Cz-D1** dye has maximum absorption peaks at 239, 288 nm and **Cz-D2** dye has maximum absorption peaks at 253, 290 nm. The absorption spectrum of **Cz-D2** dye is slightly red shifted in solution as well as in solid state due to increased effective π -conjugation length and reduced aggregation. The molar absorption coefficient at λ_{max} for **Cz-D1** and **Cz-D2** were 22,000 M⁻¹cm⁻¹ (398 nm) and 30,000 M⁻¹cm⁻¹ (401 nm) respectively. The red shift in the absorption and superior molar absorption coefficient resulted in better efficiency of **Cz-D2**.

2.2. Electrochemical properties

Energy levels (HOMO-LUMO) of dyes were investigated by cyclic voltammetry (CV) and the results are shown in Fig. 3 and relevant data are listed in Table 1. HOMO level of the photosensitizers were calculated from onset oxidation potential of dyes with Fc/Fc⁺ as internal standards (4.8 eV reference energy levels) using $E_{HOMO} = -[(Eox- E_{1/2(ferrocene)}) +$ 4.8] eV formula. Notably, the HOMO level of Cz-D1 and Cz-D2 corresponding to their first onset oxidation potential (Eox = 1.13 V) in CV, is at same energy level of -5.82 eV as carbazole donor unit is present in both the dyes. The oxidation potential of all photosensitizers versus normal hydrogen electrode (V vs NHE) is more positive than the redox potential of electrolytes, indicating that thermodynamically favorable oxidized photosensitizers can regenerate effectively. The LUMO level of photosensitizers were calculated from the onset absorption spectra of dyes ($E_{LUMO} = Eg - E_{HOMO}$), and are -3.13, and -3.27 eV for Cz-D1 and Cz-D2 dyes, respectively. The LUMO level of Cz-D2 dye is lower than Cz-D1 dye due to the increased acceptor ability. These values are above the conduction band (CB) of the TiO₂ electrode, which is necessary for sufficient driving force to inject the electrons from light-oxidized dye to CB of nanocrystaline TiO₂ surface. Based on CV results, Fig. 3b illustrates the energy level diagram of dyes. It is clear that the LUMO of Cz-D2 dye matches well with the conduction band of TiO2 and HOMO matches well with the potential of redox electrolyte (Liquid and SJE-4 electrolyte); this improves J_{sc} and results in high PCE.

2.3. Theoretical calculations of molecular orbital

The electronic distribution of frontier molecular orbitals (HOMO, LUMO) of dyes were calculated by density functional theory (DFT) using B3LYP/6-31G (d,p) basis set for optimization of dye molecules. Electronic transitions of dyes from HOMO to LUMO and other transitions



Fig. 1. Synthetic route of organic sensitizers (i) NBS, THF, 12 h, (ii) 2,3-Difluoro-4-formylphenylboronic acid, Pd(PPh₃)₄, K₂CO₃, THF:H₂O = 2:1, Aliquat, 85 °C, 18 h (iii) Cyanoacetic acid, Piperidine, CH₃CN, 85 °C, 8 h.



Fig. 2. Absorption spectra of photosensitizers Cz-D1 and Cz-D2 in CHCl₃ solution (a) and on nanocrystaline TiO₂ film (b).

 Table 1

 Photophysical, electrochemical and life time properties of carbazole based dyes.

Dye	Solution λ_{max} [nm] ^a	Film λ_{max} [nm] ^b	$\epsilon_{max} [M^{-1}]$ cm ⁻¹]	HOMO [eV] ^c	LUMO [eV] ^c
Cz- D1	239, 288, 398	417	22,000	-5.82	-3.13
Cz- D2	253,290, 401	453	30,000	-5.82	-3.27

^a Maximum absorption wavelength of dyes in chloroform solution.

 $^{\rm b}$ Maximum absorption wavelength of dyes that were absorbed onto the ${\rm TiO_2}$ films.

^c Onset potentials from CV measurements of thin films in 0.1 M Bu₄NPF₆/ CH₃CN solution, estimated from $E_{HOMO} = -\{(E_{0n}^{ov}-E_{1/2}(ferrocene)) + 4.8\}$ eV and $E_{LUMO} = E_{g}$ calculated using onset of UV (TiO₂ film)– E_{HOMO} .

were also ascertained by TD-DFT calculations performed by CAM-B3LYP/6-31G (d,p) basis set. The results of computational analysis are presented in Fig. 4 and Table 2. This analysis reveals that increasing π -spacer units and anchoring groups (mono and di anchors) results in red shift of absorption spectra and modifies the energy levels. The performance of dyes depends on planarity of back bone and charge transfer from D to A. Moreover, the acceptor moiety and length of alkyl chain also affects the dye performance. In **Cz-D1** and **Cz-D2** dyes HOMO levels are mainly located on donor segment and strongly distributed into spacer moiety whereas the LUMO levels are mainly located on acceptor and spacer unit. These results reveal that the better performance of **Cz-D2** dye might be due to the well separated HOMO and LUMO orbitals on the donor and acceptor parts, respectively. Proper separation of HOMO and LUMO orbitals is an advantage for charge migration from D to A in photo excited state of dye.

2.4. Preparation of electrolytes

The electrolyte contains solid organic ionic conductor (SJE-4, Fig. 5), iodide source (1-butyl-3-methylimidazolium iodide, BMII), iodine and TBP (*tert*-butyl pyridine). The molar proportion of composition was usually 0.03(SJE-4): 0.04 (BMII): 0.05 (I₂): 0.5 (TBP). All components were mixed in acetonitrile solvent.

2.5. Fabrication of DSSCs

The preparation of TiO_2 photoelectrode was done as per our previously reported method [22,23]. The dye solar cells were assembled by placing a Pt-coated FTO (CEs) on the (**Cz-D1 & Cz-D2**) dyes sensitized TiO_2 photo-electrode using a hot-melt Surlyn film. A solution of electrolytes in acetonitrile was injected into the interior space of the device from the predrilled holes on the Pt-based CEs and sealed using epoxy resin. In solid state devices the same procedure was followed and after filling the electrolyte, devices were kept in a vacuum oven at 50 °C for at least 6 h to remove the organic solvent. The same process was repeated three times to ensure that the TiO_2 porous film was filled with a compact layer of the SJE-4. The active area of all DSSC devices was 0.20 cm².

2.6. Photovoltaic characterization of DSSCs

The DSSCs were fabricated using **Cz-D1** and **Cz-D2** sensitizers with nanocrystalline TiO_2 anatase semiconductor as the photoanode. The DSSCs device performance parameters, such as short-circuit current



Fig. 3. (a) Cyclic voltammograms and, (b) Energy level diagram of Photosensitizers compared to the energy levels of TiO₂ and electrolytes.



Fig. 4. Frontier molecular orbital of the designed dyes.

Table 2

Selected transition energies wavelengths, their orbital contribution and oscillator strengths (*f*) for the dyes calculated using TD-DFT, CAM-B3LYP/6-31G (d, p) basis set.

Dye	λ/nm	f	Wavefunctions
Cz-D1 Dye	347	1.3211	H → L (82%)
	279	0.2239	$\rm H \rightarrow L{+1}$ (37%) H-1 \rightarrow L (21%)
	259	0.1721	H-3 → L (42%)
	233	0.1650	$H \rightarrow L+2$ (43%)
	219	0.3614	$H \rightarrow L+3$ (38%)
Cz-D2 Dye	445	0.5915	H → L (98%)
	424	0.1425	$H \rightarrow L+1$ (98%)
	383	0.1333	H-1 → L (92%)
	381	0.1975	$H-1 \rightarrow L+1$ (94%)
	325	0.1995	$\text{H-2} \rightarrow \text{L} (63\%) \text{ H} \rightarrow \text{L} (30\%)$
	318	0.3377	$H-2 \rightarrow L+1$ (89%)
	279	0.5303	$H-3 \rightarrow L$ (65%)

density (J_{sc}), fill factor (FF), open-circuit photovoltage (V_{oc}), and power conversion efficiency (PCE), were measured under 100 mW/cm² (AM 1.5) illumination, and are depicted in Table 3. The DSSCs based on **Cz-D2**, which has bis *o*,*m*-difluoro substituted Phenylene spacer and two anchoring units (-CNCH₂COOH), features J_{sc} and V_{oc} values of 10.2 mA/ cm² and 0.707 V respectively. The PCE was calculated to be 5.20% using the following equation: PCE = $P_{max}/P_{in} \times 100$. In difference, the cell based on **Cz-D1**, which has single phenylene spacer and –CNCH₂COOH



Fig. 5. Structure of solid organic ionic conductor, SJE-4 (where carbon in green, nitrogen in blue, iodide in purple, hydrogen in grey and oxygen in red) [33]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 3					
Photovoltaic parameters	of DSSCs with	solid and	liauid	electrolvt	es.

*			1	5	
Photovoltaic	Cz-D1		Cz-D2		
parameters	A	В	A	В	
$J_{\rm sc}$ (mA cm ⁻²)	7.78 ±(0.12)	6.22 ±(0.20)	$10.2\pm(0.18)$	$8.74\pm(0.25)$	
V _{oc} (V)	0.690 ±(0.05)	0.658 ±(0.06)	$\textbf{0.707} \pm \textbf{(0.05)}$	0.691± (0.10)	
FF (%)	58.0 ±(1.0)	55.0 ±(1.2)	$59.2\pm(1.0)$	$55.0\pm(1.5)$	
PCE (%)	3.95 ±(0.20)	$2.60\pm(0.22)$	$5.20\pm(0.15)$	$\textbf{4.02} \pm \textbf{(0.30)}$	

^aPerformances of DSSCs were measured with 0.20 cm² working area (measurements were performed under AM 1.5, 100 mW/cm² irradiation). J_{sc} (mA/cm²): short-circuit current, V_{oc} (V): open circuit voltage, FF (%): fill factor and PCE (%): Photo conversion efficiency, A and B indicates liquid-state and solid-state electrolyte based DSSCs respectively.

group, has a lower J_{sc} value of 7.78 mA/cm² (Fig. 6a). As per literature, the IPCE value is closely related to photocurrent density (J_{sc}) at a specific wavenumber (λ_{max}) and power input (P_{in}) [31].

$$IPCE(\%) = 1240 \times \frac{J_{sc}}{I_{0(\lambda)}\lambda(nm)} \times 100$$

To confirm the different Jsc results between Cz-D1 and Cz-D2, the IPCE values which usually depend on charge collection, light harvesting, and electron injection efficiencies were measured. Fig. 6b shows the IPCE intensity curves as a function of the incident light wavelength for the DSSCs based on the new organic sensitizers on nanocrystaline TiO₂ photoanode. Both devices can efficiently convert the light into current in the range of 350 nm-550 nm. The DSSCs containing Cz-D2 sensitizer based device exhibited a broad and higher IPCE of 66% in the range of 350-650 nm, while the Cz-D1 sensitizer based device shown blue-shift and lower IPCE of 54% in the range of 350-630 nm. The higher percentage of IPCE was observed for the sensitizer Cz-D2, which is due to its better light harvesting capacity and broad absorption in the visible region. The changes of IPCE curves are consistent with the trend of the absorption spectra on the nanocrystaline TiO₂ photoanode (Fig. 2b). In **Cz-D2** dye based device the J_{sc} and V_{oc} are improved upon substitution of the second o,m-difluoro substituted phenylene spacer and acceptor groups. It has a higher PCE because the $D-(\pi-A)_2$ system of carbazole based dye has a positive effect on IPCE curve and dye loading on TiO₂ photoanode surface (ε) compared with that of **Cz-D1** having one phenylene spacer and acceptor unit. The ε value of **Cz-D1** and **Cz-D2** were 0.74×10^{-6} and 1.23×10^{-6} mol⁻¹ cm⁻¹ respectively. The reason for higher loading of Cz-D2 is its better electronic coupling with the TiO₂



Fig. 6. (a) *J*-*V* characteristics of DSSCs based on the liquid electrolyte (inset; *J*-*V* measured in dark condition) and (b) IPCE spectra and integral current density were measured under 1 sun (100 mW/cm², AM 1.5 irradiation) light.

matrix due to the presence of two carboxylic acceptor groups.

Under similar condition we have also fabricated ss-DSSCs with **Cz-D1** and **Cz-D2** dyes and solid organic ionic conductors (SOICs) SJE-4 and the measurement was performed at a light intensity of 100 mW/cm². The results of ss-DSSCs are depicted in Fig. 7a and the corresponding photovoltaic parameters are presented in Table 3. A maximum PCE of 4.02% with J_{sc} of 8.74 mA/cm² and V_{oc} of 0.691 V were obtained for the **Cz-D2** sensitizer based ss-DSSCs. It is noted that reduced J_{sc} and V_{oc} values compared with liquid based electrolyte were obtained, and same

trend was also observed in IPCE spectra (ESI, Fig. S1). The enhanced V_{oc} value (in liquid electrolyte) may be explained in terms of the reduction in the back electron transfer from the nanocrystalline TiO₂ conduction band to the triiodide ions in the electrolyte [32].

Moreover, liquid electrolyte has easy penetration in porous TiO₂ matrix and had better interfacial contact compared to solid electrolyte. In ss-DSSCs, reduced J_{sc} was obtained because of low ion transfer via hopping or grotthuss mechanism rate is slightly lower than liquid based electrolytes [14,33,34]. Moreover, pore filling and interface connectivity of solid electrolyte might also be low with TiO2 and counter electrode, leading to a decrease in fill factors and loss of photocurrent. But the long term stability of solid state electrolytes is superior compared to liquid electrolyte based DSSCs. Liquid electrolytes have many drawbacks such as; (i) it contains highly volatile organic solvents, (ii) TiO₂ surface bound organic sensitizer after coming in contact with liquid electrolytes start desorbing, (iii) liquid electrolyte is corrosive in nature, and (iv) leakage problem, etc. [11,35,36] Therefore, in Fig. 7b, we have performed the stability analysis of liquid and solid electrolyte based DSSCs. To show the stability of the SOICs electrolyte, as mentioned in the introduction (i.e. solvent evaporation or leakage), compared to the liquid electrolyte, a comparison is carried out for four devices (two devices for each dye) fabricated and sealed in the same procedure, except one was filled with solid electrolyte and the other with liquid electrolyte. The PCEs were measured at an interval of 5 days, and after 25 days the liquid electrolyte based device displayed that most of its electrolyte in the device was evaporated, whereas the solid electrolytes based device retained its electrolyte and the PCE was pretty much unchanged. In Fig. 7b the PCE as a function of time are illustrated for a period of 25 days, it is found that the ss-DSSCs show excellent stability.

The EIS technique was used to study the internal resistance, interfacial properties and charge transfer kinetics of nanocrystalline TiO₂ layers in DSSCs [37,38]. EIS spectra were measured in dark condition using electrochemical workstation (CHI660E, CH instruments, USA). Fig. 8 shows the Nyquist plots of solid and liquid electrolytes based DSSCs. The EIS spectra can be interpreted by fitting it using equivalent circuit (Table 4), with components as explained below. Each equivalent circuit consisted of several components as shown in Fig. 8 (inset): Interfacial resistance (R_{pt}) of electron transfer at Pt-CEs/electrolyte interface, recombination resistance (R_k) in TiO₂ matrix, diffusion resistance (R_D) in electrolyte and constant phase element (CPE-P) the value of CPE-P is associated with the surface roughness and porosity of the photoelectrode [23,39,40]. Nyquist spectra of the DSSCs showed three semicircles: 1st high frequency region, represents R_{pt} ; 2nd mid frequency region, represent R_k and 3rd lower frequency region, represent



Fig. 7. (a) J-V characteristics of DSSCs based on the solid electrolyte (inset; J-V measured in dark condition) and (b) devices stability curve: PCE as a function of time.



Fig. 8. Nyquist plots for the fabricated DSSCs based on solid and liquid electrolytes with **Cz-D1** and **Cz-D2** sensitizers in the dark at V_{oc} (0.65 V) in a frequency range from 0.1 Hz to 100 kHz. (Inset: equivalent circuit model used for fitting and higher frequency zooming).

R_D. As shown in Table 4, R_{pt} of the DSSCs with liquid electrolyte is lower compared to solid electrolytes. However, R_k was higher for **Cz-D2** sensitizer with solid and liquid electrolytes based devices, compared to **Cz-D1** sensitizer based devices. The electron lifetime (τ_e) of **Cz-D2** is also higher in both solid and liquid electrolytes, while a shift of low frequency (mid) corresponds to a longer τ_e and is subjected to a higher value of V_{oc} .

Tafel polarization measurement was used to study the interfacial charge transfer properties of the electrolytes on the nanocrystaline TiO_2 matrix [41]. As discussed in our previous papers [23,42,43], the rates of anodic (β_a) and cathodic (β_c) reactions at the TiO_2 photoanode/redox mediator interface can be described by the following equation (the Buttler Volmer Equation) [44–46].

$$j = -j_0 \left(exp^{\beta_C nF} / RT(E - E_{eq}) - exp^{\beta_a nF} / RT(E - E_{eq}) \right)$$

 E_{eq} is the equilibrium potential of I^-/I_3^- electrolyte, J_0 is the current exchange density and E is the applied voltage. In dark condition the equation simplifies to $j = j_0$ as E becomes E_{eq} , also J_0 depends on the concentrations of redox couple in the electrolyte and reaction area on the TiO₂ surface. In Fig. 9, tafel analysis is illustrated which gives an insight into the electrolyte kinetics of DSSCs based on the solid and liquid electrolytes. In liquid electrolyte system, the Jo for the I^-/I_3^- redox couple at the TiO₂/electrolyte interface was about 0.69 nA/cm² (Cz-D1) and 0.82 nA/cm² (Cz-D2). It is much higher than that of the DSSCs based on the solid state electrolyte (Table 4).

The solid electrolyte resulted in a decrease of J_0 which increased the charge transfer resistance at electrolyte/TiO₂ surface. Lower β c slope value was found in the liquid electrolyte based DSSCs as shown in Fig. 9 and Table 4. These β c slope value (lower than solid electrolyte), close to 235 mV/decade (**Cz-D1**) and 220 mV/decade (**Cz-D2**), corresponds to the recombination reaction at the sensitized TiO₂ photoanode/I⁻/I₃ electrolyte interface between electrons from the CB of titania and triiodide in the liquid electrolyte. The reduced β c slope indicates an enhanced reaction of the triiodide at the sensitized TiO₂ photoanode/I⁻/I₃ electrolyte interface.

Table 4

Electrochemical parameters of DSSC with liquid and solid electrolyte.

3. Conclusion

In conclusion, we have developed o,m-difluoro substituted Phenylene spacer and carbazole based dyes Cz-D1 and Cz-D2, consisting monoand di-anchoring groups. Both dyes exhibited interesting optical, electrochemical and photovoltaic properties. The absorption spectra of planar Cz-D1 dye show strong H-aggregation in solution and dye absorbed on TiO₂. Cz-D2 contain two electron acceptor groups and nonplanarity ensuing less aggregation, provide efficient electron extraction from carbazole donor, high molar extinction coefficient, better charge transfer and lower LUMO level resulted in better photovoltaic performance than Cz-D1, in presence of liquid (BMII) as well as solid SJE-4 electrolyte systems. Without using any additives, Cz-D2 and Cz-D1 exhibited attractive power conversion efficiency of 5.35% and 4.15%, respectively in presence of Iodide redox electrolyte. Both o,m-difluoro substituted dyes exhibited less efficiency in presence of SJE-4 solid electrolyte system due to the aggregation between fluorine substituted phenylene spacer and electrolyte through strong H-bonding and resulted in more electron recombination/back electron transfer as confirmed by TD-DFT and EIS measurements. PCE as a function of time for a period of 25 days were also recorded, the mono anchoring Cz-D1 device exhibits better stability than di anchoring Cz-D2 in presence of both electrolyte systems.

4. Experimental

4.1. Reagents, materials and methods

All required chemicals used for the synthesis of dyes were purchased from sigma Aldrich, TCI and were used without any further purification unless otherwise explained. Nano-crystalline TiO₂ (<20 nm, 99.8%, anatase), alpha-terpineol, ethyl cellulose, titania (IV) propoxide, TiCl₄, BMII and *tert*-butyl pyridine were purchased from Sigma-Aldrich (India) and used as received. Acetonitrile and ethanol were purified using the standard process. Fluorine tin oxide glass (FTO, 12 Ω /sq, Solaronix, SA, Switzerland) and sealing materials (Meltronix tape, thickness 60 µm)



Fig. 9. Tafel polarization study of the solid and liquid electrolytes based DSSCs fabricated using new dyes.

Device	State of the Electrolyte	$R_{pt} \left(\Omega \right)^{a}$	$R_k (\Omega)^a$	CPE-P (%) ^a	τ (ms) ^a	$\beta a (mV/decade)^b$	$\beta c (mV/decade)^{b}$	J _o (nA/cm ²) ^b
Cz-D1	Liquid	20.9	229	65	0.83	145.5	235.4	0.69
Cz-D2	Liquid	21.9	323	69	1.68	115.6	220.0	0.82
Cz-D1	Solid	25.1	210	70	0.80	122.4	259.5	0.21
Cz-D2	Solid	24.6	265	70	1.15	115.4	308.3	0.32

^a Electrochemical Impedance spectroscopy.

^b Data obtained from Tafel polarization curve.

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were used for the fabrication of the DSSC device. The alkylation and bromination of carbazole were done according to the published literature procedure [22,23]. The synthetic procedures of two dyes (**Cz-D1**, **Cz-D2**) are shown in Fig. 1. By using Suzuki coupling reaction, CZ-PhF2-CHO and Cz-2PhF2-CHO were synthesized. The final step to synthesize new dyes (**Cz-D1**, **Cz-D2**) was performed by using Knoevenagel condensation reaction method. All the necessary products were purified by column chromatography, characterized by NMR (¹H, ¹³C) and HRMS spectrometry. Instruments used for different characterization purpose and the characterization data are described in supporting information (ESI Page S2–S9).

4.2. General synthetic procedure of aldehyde

4.2.1. Synthesis of Cz-PhF2-CHO

A 2 M K₂CO₃ solution in THF: H₂O (2:1) was added to the mixture of 3-bromo-9-octyl-9H-carbazole (0.2 mmol) and 2,3-Difluoro-4-formylphenylboronic acid (0.3 mmol) then degassed properly. Finally, in presence of argon, Pd(PPh₃)₄ (2 mol%) was added and heated to 85 °C for 18 h. Then the solution was evaporated under reduced pressure. The extracted compound was washed with chloroform and aqueous brine solution. Finally, organic part was dried with anhydrous MgSO₄. The desired product was purified by column chromatography (silica gel, EtOAc-hexane 1:2 as eluent).

4.2.2. Synthesis of Cz-2PhF2-CHO

In a clean reaction flask 3,6-dibromo-9-octyl-9H-carbazole (0.2 mmol) and 2,3-Difluoro-4-formylphenylboronic acid (0.5 mmol) taken. Then, 2 M K₂CO₃ solution in THF: H₂O (2:1) was added to the reaction mixture. Finally, in presence of argon, Pd(PPh₃)₄ (2 mol%) was added and heated to 85 °C for 18 h. Then the solution was evaporated under reduced pressure. The extracted compound was washed with chloroform and aqueous brine solution. Finally, organic part was dried with anhydrous MgSO₄. The desired product was purified by column chromatography (silica gel, EtOAc-hexane 1:2 as eluent).

4.3. General synthetic procedure of dyes

4.3.1. Synthesis of Cz-D1

The solution of acetonitrile: chloroform (2:1) was added to the mixture of Cz-PhF2-CHO (0.2 mmol) and cyanoacetic acid (0.3 mmol) and degassed it thoroughly. Finally, in presence of argon atmosphere the piperidine (catalytic amount) was added into the solution. Then the solution was refluxed for 18 h. After cooling to RT, the solution was evaporated under reduced pressure. Extracted compound was washed with chloroform and 0.1 M aq. HCl. Then the organic part was dried with MgSO₄. The product was purified by conventional column chromatography (silica gel, EtOAc -hexane 1:2 as eluent) and it was obtained as a yellow-orange solid.

4.3.2. Synthesis of Cz-D2

The solution of acetonitrile: chloroform (2:1) was added to the mixture of Cz-2PhF2-CHO (0.2 mmol) and cyanoacetic acid (0.5 mmol) and degassed it thoroughly. Finally, in presence of argon atmosphere the piperidine (catalytic amount) was added into the solution. Then the solution was refluxed for 18 h. After cooling to RT, the solution was evaporated under reduced pressure. Extracted compound was washed with chloroform and 0.1 M aq. HCl. Then the organic part was dried with MgSO₄. The product was purified by conventional column chromatography (silica gel, EtOAc -hexane 1:2 as eluent) and it was obtained as a yellow-orange solid.

4.3.3. 2,3-Difluoro-4-(9-octyl-9H-carbazol-3-yl)benzaldehyde [Cz-PhF2-CHO]

Yield = 70%, ¹H NMR (400 MHz, CDCl₃): δ (ppm) 10.37 (s, 1H), 8.33 (s, 1H), 8.15–8.13 (d, 1H), 7.71–7.69 (t, 3H), 7.53–7.50 (t, 2H),

7.49–7.44 (m, 3H), 7.30–7.27 (d, 1H), 4.33 (t, 2H) 1.91–1.89 (t, 2H), 1.42–1.32 (m, 5H), 1.30–1.24 (m, 9H), 0.89–0.86 (t, 3H). 13 C NMR (100 MHz, CDCl₃): δ (ppm) 186.14, 154.73, 152.88, 149.15, 146.89, 141.12, 140.93, 138.34, 126.65, 126.48, 125.65, 121.33, 120.70, 119.64, 109.27, 109.17, 43.47, 31.99, 29.56, 29.37, 29.19, 27.51, 22.80, 14.26. HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₂₇H₂₈F₂NO 420.2139, found 420.2123.

4.3.4. 4,4'-(9-octyl-9H-carbazole-3,6-diyl)bis(2,3-difluoro benzaldehyde) [Cz-2PhF2-CHO]

Yield = 68%, ¹H NMR (400 MHz, CDCl₃): δ (ppm) 10.37 (s, 1H), 8.37 (s, 1H), 7.75–7.64 (m, 4H), 7.56–7.53 (d, 2H), 7.48–7.46 (m, 4H), 4.37 (t, 2H) 1.94–1.92 (t, 2H), 1.56 (t, 1H), 1.44–1.25 (m, 9H), 0.89–0.84 (t, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 186.13, 141.39, 137.31, 132.32, 128.79, 128.71, 127.34, 125.66, 123.31, 123.06, 121.51, 114.13, 109.61, 43.69, 31.96, 29.89, 29.54, 29.35, 27.49, 22.78, 14.24, 14.26. HRMS (ESI) *m/z*: [M]⁺ calcd for C₃₄H₂₉F₄NO₂ 559.2134, found 559.2141.

4.3.5. (Z)-2-Cyano-3-(2,3-difluoro-4-(9-octyl-9H-carbazol-3-yl)phenyl) acrylic acid [Cz-D1]

Yield = 73%, ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 8.86–8.42 (d, 2H), 8.30 (s, 1H), 8.24–8.22 (d, 2H), 8.10 (S, 2H), 8.02 (s, 1H), 7.71–7.70 (m, 4H), 7.62.7.61 (m, 6H), 7.56–7.48 (m, 7H), 7.23 (m, 3H), 4.41 (t, 2H), 1.57 (m, 5H), 1.33–1.15 (t, 6H), 0.84–0.78 (m, 4H), 1.30–1.24 (m, 9H), 0.89–0.86 (t, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆): δ (ppm) 149.54, 148.03, 146.33, 140.51, 140.06, 136.79, 133.09, 126.47, 126.22, 125.59, 123.84, 122.94, 122.44, 122.04, 121.42, 120.95, 120.63, 119.19, 118.64, 109.58, 50.91, 30.99, 28.51, 27.22, 26.14, 24.16, 22.03, 13.85. HRMS (ESI) *m/z*: [M – H]⁻ calcd for C₃₀H₂₈F₂N₂O₂ 485.2041, found 485.2031.

4.3.6. (2Z,2'E)-3,3'-((9-octyl-9H-carbazole-3,6-diyl)bis(2,3-difluoro-4,1-phenylene))bis(2-cyanoacrylic acid) [Cz-D2]

Yield = 68%, ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.32–8.18 (m, 2H), 7.92 (s, 1H), 7.75–7.68 (m, 3H), 7.56–7.40 (m, 3H), 7.17–7.10 (d, 2H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 149.10, 146.82, 140.39, 133.99, 132.19, 128.92, 126.29, 122.99, 122.73, 121.16, 120.68, 117.88, 117.06, 114.29, 109.39, 108.64, 51.17, 31.91, 29.88, 29.15, 27.32, 26.57, 22.74, 14.23. MALDI-TOF *m/z*: [M – 2H]⁺ calcd for C₄₀H₃₁F₄N₃O₄ 691.6696, found 691.6610.

Declaration of competing interest

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2019.108021.

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