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## ARTICLE

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Metal-free dithiafulvalene (DTF) organic sensitizers for dye-sensitized solar cell (DSSC) applications have been greatly improved and expanded in the last decade. Herein, we modified basic carbazole (CBZ) sensitizer (CO) by substituted an additional excellent donor hexyl dithiafulvalene (HDT) and synthesized two dithiafulvalene-carbazole (DTF-CBZ) using D-π-A concept in which either cyanoacrylic acid (HDT-C1) or rhodanine-3-acetic acid (HDT-C2) as acceptor or anchoring group for DSSC applications. All the synthesized sensitizers were characterized by various spectroscopic, electrochemical techniques and successfully applied in DSSCs using I<sup>-</sup>/I<sub>3</sub><sup>-</sup> liquid redox couple. UV-Visible absorption, electrochemical studies and theoretical calculations (DFT/TDDFT) suggest that favoured energy levels for the sensitization of nanocrystalline TiO2. The power conversion efficiency (PCE) of these two dyes compared with simple carbazole sensitizer (CO), the PCE improved significantly from 3.96% (CO) to 7.38% (HDT-C1) and 6.90% (HDT-C2). The superior performance due to the introduction of strong electron donating hexyl dithiafulavalene group, it leads to minimizing the aggregation and also favoured quick regeneration of oxidized dye from redox couple in DSSCs. The PCE of HDT-C2 is not drastically reduced as compared to HDT-C1 probably due to well match HOMO level with the redox potentials of redox couple. This thermally stable DTF-CBZ organic dyes possess the excellent photovoltaic property and anticipated towards the alternatives of existing materials in DSSCs applications and it will be active methodology would make DTF sensitizers in this broad and quickly growing area of metal-free organic sensitizers in solar cells.

### Introduction

Dye-sensitized solar cells (DSSCs) have attracted a wide-range of attention in both academic and industry after motivating work by O'Regan and Grätzel in 1991(using Ru(II) polyridyl complex as a dye with  $I^{-}/I_{3}^{-}$  redox couple showed an efficiency of 7.1%.<sup>1</sup> Over a period of couple of decades the certified efficiency of DSSC has reached to 11.9% with Ru(II) polypyridyl complex as dye with traditional  $I^{-}/I_{3}^{-}$ redox couple and device efficiency has reached 14.3% using metalfree organic dye i.e., ADEKA-1 sensitizer using Co(II/III) as redox couple.<sup>2-4</sup> Despite showing such fancy efficiencies, the metal-free organic sensitizer should require easy to synthesize, low-cost, less harmful materials, thermally and photo-chemically stable. Among the metal-free organic sensitizers, the most proficient tactic was based on D- $\pi$ -A, leading to a broad and intense optical absorption band in the visible spectral region due to effective intramolecular charge transfer (ICT) from D to A units.<sup>5-10</sup> Quite a few organic sensitizers have been reported in the literature using  $D-\pi-A$ approach for application in DSSCs, such as coumarin dyes<sup>11,12</sup> indoline dyes,<sup>13-15</sup> triarylamine dyes,<sup>16-19</sup> carbazole dyes,<sup>20-24</sup>

<sup>a</sup>Polymers & Functional Materials Division, CSIR-Indian Institute of Chemical Technology, Uppal Road, Tarnaka, Hyderabad 500607, India, E-mail: siribabu@iict.res.in phenothiazine (PTZ),<sup>25-29</sup> and diketopyrrolopyrrole (DPP) dyes,<sup>30-32</sup> etc. The champion device efficiency obtained till now is based on carbazole scaffold and indeed the sensitizer played a vital role along with redox mediator.<sup>4</sup> Recently, academicians paid attention to thermally stable strong electron donor dithiafulvalene (DTF) based scaffold organic sensitizers mainly due to straightforward synthesis, low cost, and easy to optimize its optical and electronic properties to suit DSSC applications.

Dithiafulvalene (DTF) as a strong terminal electron donor has been used in high success DSSCs due to its non-planar molecular configuration that facilitates to minimize the formation of aggregates on the surface of nanocrystalline TiO<sub>2</sub>.<sup>33-35</sup> DTF sensitizers facilitate the ultrafast interfacial electron injection from excited state of sensitizer to the conduction band (CB) of semiconductor.<sup>36</sup> Secondly, the recombination of injected electrons with the redox couple can be concealed because of the propellershaped DTFs molecular structure. Besides, the oxidized DTFs unit is spatially conveniently placed to support the move of electrons towards the redox couple species, ensuring fast dye regeneration. Dithiafulvalene (DTFs) exhibit unique charge transport characteristics due to their coplanar molecular structures with strong π-π\* and S–S interfaces.<sup>37</sup>

Shihe yang and co-workers for the first time investigated the sensitization of nanocrystalline TiO<sub>2</sub> using metal-free organic DTF sensitizers by adopting D- $\pi$ -A concept.<sup>38</sup> In all three sensitizers

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keeping the same donor (DTF) and acceptor or anchoring cyanoacrylic acid group with varying  $\pi$ -bridges or spacers such as phenyl, biphenyl and phenyl-thiophene-phenyl that displayed photon conversion efficiency (PCE) from 3.15% to 8.29% with IPCE of 85% using  $I^{-}/I_{3}^{-}$  liquid redox couple, which is highest till now using DTF based dyes. The improved efficiency is due to increase of both short-circuit current density  $(J_{sc})$  and open-circuit voltage  $(V_{oc})$  with increasing auxiliary acceptor  $\pi$ -bridge length. These results suggest that the increasing the  $\pi$ -bridge length not only shifts the absorption maxima with enhanced molar extinction coefficients but also improve overall efficiency of the device. Thereafter a few groups have started working on DTF based sensitizers using D- $\pi$ -A concept in which the  $\pi$ -spacers are triphenylamine, phenothiazine and cyclopenta[2,1-b:3,4-b']dithiophene have been used but efficiencies are in the range of 3 to 7%.<sup>39-44</sup> In an extension of our efforts towards the development of thermally stable and efficient metal-free organic dyes, we realized that the introduction of carbazole moiety as  $\pi$ -spacer, DTF as donor and either cyanoacrylic acid or rhodanine-3-carboxylic acid as an acceptor moiety may give better efficiency to DSSC devices. Carbazole derivatives are widely used in several optoelectronic applications based on their optical and electronic properties and still, no reports are available based on HDT-CBZ sensitizers for DSSC applications to the best of our knowledge. In this work, we have introduced strong electron donor 4,5-bis(hexylthio)-1,3-dithiole-2-thione (HDT) at C6 position of carbazole and either cyanoacrylic acid (HDT-C1) or rhodanine-3acetic acid (HDT-C2) as an acceptor or anchoring group in these sensitizers. In addition to this, we have also synthesized a sensitizer having cyanoacrylic acid anchoring group at C3 position of carbazole as pristine (CO) sensitizer for comparison. All three sensitizers are characterized by various spectroscopic and electrochemical methods. Finally, the new sensitizers applied for the sensitization of nanocrystalline TiO<sub>2</sub> using  $I^{-}/I_{3}^{-}$  redox couple in acetonitrile solvent and found efficiencies up to 7.38%. The structures of Dithiafulvalene-Carbazole based (C0, HDT-C1 and HDT-C2) sensitizers are shown in Chart1.



**Chart 1.** Molecular structures of Dithiafulvalene-Carbazole based **(C0, HDT-C1** and **HDT-C2**) sensitizers.

### 2. Experimental Section

**2.1. Materials and reagents.** All chemicals, reagents and solvents are procured either from Sigma-Aldrich or from TCI. Analytical reagent (AR) grade solvents were used for the reactions while laboratory reagent (LR) grade solvents were used for purifications and column chromatography. All the reactions were carried out under nitrogen or argon atmosphere using dry and degassed solvents.

### 2.1. Synthesis

9-(2-ethylhexyl)-9H-carbazole (1), C9-(2-ethylhexyl)-9H-Carbazole 3carbaldehyde (2), 9-(2-ethylhexyl)-9H-carbazole-3,6-dicarbaldehyde (3), and 4,5-bis(hexylthio)-1,3-dithiole-2-thione (HDT) were synthesized according to the literature procedure.<sup>7,45,46</sup>

2.2.1. Synthesis 6-((4,5-bis(hexylthio)-1,3-dithiol-2of ylidene)methyl)-9-(2-ethylhexyl)-9H-carbazole-3-carbaldehyde (4) Was synthesized modified literature procedure.<sup>7</sup> Compound (3) (0.7 g, 1.969 mmol) and 4,5-bis(hexylthio)-1,3-dithiole-2-thione (HDT) (0.722 g, 1.969 mmol) were suspended in 15 mL of toluene and 10 mL of triethyl phosphite. The reaction mixture was refluxed for 2 hours. After cooling to room temperature, the solvent was removed by rotary evaporator and the resultant residue dissolved in chloroform. The mixture was washed with brine and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. Solvents were removed by rotary evaporation and the residue was purified by silica gel column chromatography with Hexane: DCM (10: 1, v: v) as eluent to afford (4) as yellow oil. Yield: 48.0%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.09 (s, 1H), 8.55 (d, J = 1.4 Hz, 1H), 8.26 (d, J = 1.9 Hz, 1H), 8.08 - 8.01 (dd, J = 8.6, 1.6 Hz, 1H), 7.62 - 7.58 (dd, J = 8.7, 1.9 Hz, 1H), 7.48 - 7.44 (d, J = 8.6 Hz, 1H), 7.33 - 7.28 (m, 1H), 6.27 (s, 1H), 4.24 - 4.20 (d, J = 7.6, 2H), 2.86 - 2.75 (t, J = 7.1 Hz, 4H), 1.68 - 1.42 (m, 4H), 1.37 - 1.18 (m, 21H), 0.95 - 0.89 (m, 6H), 0.86 - 0.75(m, 6H). MALDI-TOF: (m/z) found 654.9619 (calculated 654.1).

**2.2.2. General procedure for the synthesis of CO and HDT-C1:** Under N<sub>2</sub> atmosphere, the mixture of corresponding aldehyde (2 or 4) (1 mmol), cyan acetic acid (5 mmol) and ammonium acetate (3 mmol) were dissolved in 10 mL of acetic acid and refluxed for 18 hours. The reaction was monitored by TLC and at the end of reaction, the reaction mixture poured onto ice-cold water and extracted with chloroform. Collected organic layers were evaporated and dried. Then they obtained solid compound was purified by column chromatography using silica gel, stationary phase with Hexane: THF (10:1) as the eluent to give corresponding **CO** and **HDT-C1**.

**2.2.2.1. (Z)-2-cyano-3-(9-(2-ethylhexyl)-9H-carbazol-3-yl)acrylic acid (C0)**: Yield: 75%; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.53 (d, *J* = 1.2 Hz, 1H), 8.26 (d, *J* = 1.8 Hz, 1H), 8.08 – 8.01 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.82 (s, 1H), 7.66 – 7.60 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.55 – 7.49 (d, *J* = 8.6 Hz, 2H), 7.41 – 7.30 (m, 1H), 4.21 – 4.16 (d, *J* = 7.6 Hz, 2H), 1.45 – 1.15 (m, 9H), 0.97 – 0.77 (m, 6H). anal. calc. for C<sub>24</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub> (374.48): C 76.98, H 7.00, N 7.48; found: C 76.95, H 7.01, N 7.50. ESI-Mass: *(m/z)* found 375 (calculated 374.2).

**2.2.2.** (**Z**)-**3**-(**6**-((**4**,**5**-bis(hexylthio)-1,**3**-dithiol-**2**-ylidene)methyl)-**9**-(**2**-ethylhexyl)-**9**H-carbazol-**3**-yl)-**2**-cyanoacrylic acid (HDT-C1): Yield: 62%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.48 (d, *J* = 1.4 Hz, 1H), 8.20 – 8.18 (d, *J* = 4.9 Hz, 1H), 7.96 (s, 1H),7.59 – 7.55 (d, *J* = 8.2 Hz, 1H), 7.46 – 7.39 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.27 (m, 1H), 6.34 (s, 1H),4.48 – 4.43 (d, *J* = 7.8, 2H), 2.78 – 2.72 (t, *J* = 7.4 Hz, 4H), 1.57 – 1.32 (m, 4H), 1.29 – 0.98 (m, 21H), 0.82 – 0.73 (m, 12H). anal. calc. for C<sub>40</sub>H<sub>52</sub>N<sub>2</sub>O<sub>2</sub>S<sub>4</sub> (721.11): C 66.63, H 7.27, N 3.88; found: C 66.66, H 7.25, N 3.90. MALDI-TOF: (*m/z*) found 722.14 (calculated 721.1).

2.3.3. Synthesis of (E)-2-(5-((6-((4,5-bis(hexylthio)-1,3-dithiol-2ylidene)methyl)-9-(2-ethylhexyl)-9H-carbazol-3-yl)methylene)-4oxo-2-thioxothiazolidin-3-yl)acetic acid (HDT-C2): We have adopted similar synthetic procedure of CO and HDT-C1, but only difference is that here we have taken rhodanine-3-acetic acid

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(i) POCl<sub>3</sub>, DMF, 1,2-dichloreethane, (ii) HDT, P(OEt)<sub>3</sub>, Toluene (iii) Cyanoacetic acid, CH<sub>3</sub>COONH<sub>4</sub>, CH<sub>3</sub>COOH, (iv) Rhodanine-3-acetic Acid, CH<sub>3</sub>COONH<sub>4</sub>, CH<sub>3</sub>COOH

Scheme 1. Synthetic route for C0, HDT-C1 and HDT-C2 sensitizers.

instead of cyanoacrylic acid. Yield: 65%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.49 (d, J = 1.2 Hz, 1H), 8.15 – 8.20 (d, J = 4.6 Hz, 1H), 7.92 (s, 1H), 7.62 – 7.58 (d, J = 8.4 Hz, 1H), 7.42 – 7.37 (d, J = 8.2 Hz, 2H), 7.32 – 7.27 (m, 1H), 6.46 (s, 1H), 4.78 (s, 2H),4.40 – 4.36 (d, J = 7.6, 2H),3.02 – 2.88 (t, J = 7.2 Hz, 4H), 1.55 – 1.40 (m, 4H), 1.34 – 1.08 (m, 21H), 0.89 – 0.72 (m, 12H). anal. calc. for C<sub>42</sub>H<sub>54</sub>N<sub>2</sub>O<sub>3</sub>S<sub>6</sub> (827.27): C 60.98, H 6.58, N 3.39; found: C 61.00, H 6.60, N 3.40. MALDI-TOF: (*m/z*) found 826.95 (calculated 826.2).

### 2.3. Characterization

Proton (<sup>1</sup>H) NMR was recorded by using 400 MHz Bruker Avance NMR spectrometer with X-WIN NMR software. The samples were prepared either with CDCl<sub>3</sub> or CD<sub>2</sub>Cl<sub>2</sub> according to their solubility and the concentration was  $1.0 \times 10^{-3}$  M. The spectra were analyzed using Mestrenova software. ESI (Electrospray Ionization) mass spectra were recorded on a Water Quattro micro (Water Inc, USA). Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry performed on Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Reflectron-HiRes, Power: 85. Major fragmentations are given as percentages relative to the base peak intensity. Cyclic voltammetric measurements were performed on a system controlled CH instruments model CHI 620C electrochemical analyzer using 1 mM sample solution in tetrahydrofuran solvent using 0.1 M Tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte at a scan rate of 100 mV/s. The working electrode is glassy carbon, standard calomel electrode (SCE) is used as a reference electrode, and platinum wire is a counter electrode. After a cyclic voltammogram (CV) was recorded, ferrocene was added, and other voltammogram was measured. Mettler Toledo TGA/SDTA 851e instrument was used for the Thermogravimetric measurements at heating rate 10 °C min<sup>-1</sup> with 10 mg of sample. The detailed instrumentation characterization (UV-Visible absorption, time-resolved fluorescence measurements, theoretical calculations (DFT/TDDFT) and device fabrication measurements of these dyes are available in supporting information.

### 3. Results and Discussion

### 3.1. Synthesis

The detailed synthetic route of dithiafulvalene-carbazole based sensitizers is showed in Scheme 1. The intermediate compounds 1, 2 and 3 were accomplished as per literature methods.<sup>7,45,46</sup> The vital intermediate *i.e.*, compound (4) was synthesized by adopting our previously reported procedure and we adopted Knoevengel condensation of formyl derivates with either cyano acetic acid or rhodanine-3-acetic acid using ammonium acetate and acetic acid. Finally the desired sensitizers (C0, HDT-C1 and HDT-C2) were obtained by silica gel column chromatography purification. All intermediate compounds and three sensitizers were fully characterized by various spectroscopic techniques and electrochemical methods. The MALDI-TOF spectrum of HDT-C1 showed a peak at m/z = 722.14 (CHN) and HDT-C2 at m/z = 826.95, which was assigned to their comparable molecular ion peaks (Figure S1 and S8). <sup>1</sup>H NMR spectra of C0, HDT-C1 and HDT-C2 sensitizers are shown in Figure S1 to S8 (ESI).

### 3.2. Optical and Electrochemical Properties



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The optical properties are essential in order to know the sensitizers to absorb photons and that converts it into electrical energy. For this reason, we have measured the absorption properties of CO, HDT-C1 and HDT-C2 in THF solvent. Figure 1a demonstrates the absorption spectra of all three sensitizers and their corresponding wavelength of absorption maxima and molar extinction coefficients data are given in Table 1. The absorption spectrum of each of sensitizer consists of two prominent peaks in 300-500 nm and around 550 nm regions. The absorption peaks at 320 and 386 nm in the case of **CO** sensitizer purely belong to  $\pi$ - $\pi$ \* transitions of carbazole moiety as in this sensitizer not having a DTF donor whereas, in the case of HDT-C1, the peak at this region is a combination of both donor DTF and  $\pi$ -spacer carbazole. In contrast, the absorption peak red-shifted to 435 nm in case of HDT-C2 sensitizer because of the presence of powerful electron withdrawing rhodanine-3-acetic acid. In addition to this, the absorption peak at longer wavelength region at ~550 nm is feasible to intramolecular charge transfer (ICT) bands corresponding to donor DTF to the acceptor (cyanoacrylic acid or rhodanine-3-acetic acid) through carbazole  $\pi$ -spacer. Figure 1b illustrates the absorption properties of these D- $\pi$ -A acceptor dyes adsorbed on surface of the 6µm thick TiO<sub>2</sub> films. The absorption spectra of all three sensitizers are exhibit red-shifted in comparison with solution spectra in view of the fact that the interaction of the carboxylic acid group with TiO<sub>2</sub> and also possibly because of aggregation. In both the dyes the onset of absorption extends up to 650 nm. The emission spectra were measured in THF solvent at room temperature for CO, HDT-C1 and HDT-C2 dyes, which show emission maxima at 446, 460 and 498 nm, respectively. The emission intensity almost quenched when adsorbed on TiO<sub>2</sub>. The singlet excited-state lifetimes were measured in THF solvent, and they found in the range of 0.86-0.21 ns (Figure S9), and the excited lifetimes were guenched when adsorbed on TiO<sub>2</sub>. The guenching of both steady-state emission and excited-state lifetime on TiO<sub>2</sub> is presumably because of photoinduced electron transfer from singlet state of dye to the conduction band of TiO2. In the end, we calculated the singlet excited energies ( $E_{0-0}$ ), which are useful in calculating excited state oxidation potentials that will be discussed in presiding section from the intersection of absorption and emission spectra, and they are found 2.98±0.05, 2.99±0.05 and 2.61±0.05 eV for C0, HDT-C1 and HDT-C2, respectively.



**Figure 2.** Differential voltammograms of **C0, HDT-C1** and **HDT-C2** in THF using 0.1 M TBAP.

Subsequently, we measured the redox potentials of all three sensitizers in THF solvent by using differential pulse voltammetric

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technique, which will be useful for the estimation of HOMO and LUMO positions of dyes and the data presented in Jable AD From Figure 2 and Table 1 it suggests that the sensitizer CO has quasireversible oxidation peak at 1.12 V vs. NHE whereas in case of HDT-C1 and HDT-C2 the oxidation peak cathodically shifted to ~0.75 V vs. NHE. The first oxidation potential of these DTF donor based dyes was used to calculate the HOMO position and the LUMO was estimated by subtracting the band gap from its HOMO level. The found energy levels of these newly synthesized sensitizers are appropriate for the TiO<sub>2</sub> and electrolyte energy levels.<sup>47</sup> The HOMO and LUMO energy levels (vide infra) calculated by both experimental and theoretical are in good agreement with each other. Finally, we used the expression  $E_{OX}^* = E_{OX} - E_{0-0}$  is used to assess excited-state oxidation potentials (Eox\*) levels of CO, HDT-C1 and HDT-C2 dyes, which were estimated to be 1.86, 2.23 and 2.06 eV. respectively.

#### Table 1. Photophysical properties of C0, HDT-C1 and HDT-C2 dyes.

Dye	λ <sub>max</sub> <sup>a</sup> (nm)/ (ε x 10 <sup>4</sup> M <sup>-1</sup> cm <sup>-1</sup> ) (in Solution)	λ(abs. edge on TiO <sub>2</sub> )ª (nm)	λ <sub>em</sub> b nm	E <sub>1/2</sub> V vs. NHE			Lifetime
				OXc	E <sub>0-0</sub> ď (eV)	E <sub>Ox</sub> <sup>*d</sup>	(τ) (in ns), (A %)
C0	320 (4.157) 386(5.936)	435	446	1.12	2.98	1.86	0.89
HDT-C1	320 (3.176) 380 (3.382) 551 (1.150)	529	434 <i>,</i> 460	0.76, 0.99, 1.14	2.99	2.23	0.34 (86) 1.52 (14)
HDT-C2	345 (2.689) 430 (5.699) 552 (1.012)	538	498	0.75, 0.99, 1.15	2.61	2.06	0.21 (89) 1.06 (11)

<sup>a</sup>Absorption spectra were recorded in THF solution, Error limits:  $\lambda_{max}$ , ±1 nm,  $\varepsilon$  ±10%. <sup>b</sup>Solvent: THF,  $\lambda_{max}$ , ±1 nm. <sup>c</sup>Solvent: THF, Error limits: E<sub>1/2</sub> ±0.03 V, 0.1 M TBAP. <sup>d</sup>E<sub>0x</sub><sup>\*</sup> = E<sub>0.0</sub>-OX; Error limits: ±0.05 eV. All life times are in nanoseconds (ns), at  $\lambda$ ex = 458 nm.

#### 3.2. Theoretical Studies

The optimized energy structures, electronic distribution, molecular electrostatic potential (MEP) maps, theoretical absorption spectra, HOMO-LUMO energy levels, and bandgap of sensitizers (Figure 3, Table S1, S2) were theoretically calculated using the Gaussian 09 program package with the functional basis set of the B3LYP/6-31 G (d,p) level. From Table S1, it suggests that both HRD-C1 and HRD-C2 dyes have similar optimized structures in which the hexyl group on the sulfur atom of DTF donor and on the 9-N of carbazole are in the same plane which will not only minimize the aggregation but enhance the solubility of sensitizers in common organic solvents. Figure 3 and Table S1 suggests that the HOMOs for C0, HDT-C1 and **HDT-C2** dyes are completely located on the donor and  $\pi$ -spacer (DTF and carbazole) units whereas LUMO delocalized over the carbazole and cyanoacrylic acid group in CO dye. On the other hand, the LUMO delocalized completely on anchoring cyanoacrylic acid (HDT-C1) and rhodanine-3-acetic acid (HDT-C2) and partially on carbazole moiety, which indicates an efficient intramolecular electron injection from singlet excited state of the dye to conduction band of TiO2. This has been proved even from MEP maps, for both dyes, the positive electrostatic potential was at the donor DTF and  $\pi$ -spacer connecting the carbazole; while negative potential was concentrated at anchoring group either cyanoacrylic acid or rhodanine-3-acetic acid. The HOMO-LUMO gap of these dyes is 3.34, 2.74 and 2.57 eV for CO, HDT-C1 and HDT-C2, respectively. Additionally, we subjected to single-point TDDFT

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studies (first 15 vertical singlet-singlet transitions to obtain the absorption spectra) (see Figure S10) with THF as the solvent and calculated vertical excitation energies for the singlet together with oscillator strengths, as listed in Table S2. The experimental absorption properties with the theoretical data expose that the results are in excellent agreement with experimental values.



**Figure 3.** Energy diagram of **C0**, **HDT-C1** and **HDT-C2** sensitizers calculated by Gaussian 09 program package with functional basis set of B3LYP/6-31 G (d, p) level.

#### 3.3. Photovoltaic performances

At first, we have calculated the amount of sensitizer adsorbed on the surface of TiO<sub>2</sub>. This has been executed by desorbing the adsorbed dye and the obtained amounts are listed in Table 2. The loaded amounts of C0, HDT-C1 and HDT-C2 dyes are found to 4.13 x  $10^{-7}$ , 4.06 x  $10^{-7}$  and 3.99 x  $10^{-7}$  mol cm<sup>-2</sup>, respectively. The dye loading amounts of HDT-C2 low, when compared to HDT-C1 dye, probably due to the larger molecular size former dye and weak interaction with nanocrystalline TiO<sub>2</sub> surface compared to HDT-C1. The photovoltaic accomplishment of all three sensitizers i.e., the incident photo-to-current conversion efficiency (IPCE) and photocurrent-voltage (J-V) curves, was evaluated in test devices using TiO<sub>2</sub> films of 8  $\mu$ m thick with a volatile acetonitrile based electrolyte composition of 0.5 M Lil, 0.05 M I<sub>2</sub>, 0.5 M TBP (4-tertbutyl pyridine), and 0.5 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII). The detailed device fabrication was portrayed in our preceding studies.<sup>7,25</sup> Figures 4a and 4b illustrate both *I-V* and IPCE spectra of all three sensitizers and respective photovoltaic data are presented in Table 2. As seen in Table 2, the carbazole sensitizer (CO) without DTF donor have a low short-circuit current  $(J_{sc})$  of 7.22±0.37 mA/cm<sup>2</sup> whereas in case of sensitizers are having DTF donor i.e., HDT-C1 and HDT-C2 has enhanced to 14.12±0.43 and 13.19 $\pm$ 0.46 mA/cm<sup>2</sup>, respectively. The open-circuit voltage ( $V_{oc}$ ) and fill factor of all three sensitizers are in the range of 0.76±0.02 to 0.78±0.02 V and 0.67 to 0.72, respectively. These results clearly suggest that the presence of donor DTF has improved photovoltaic performance and device efficiency of sensitizer CO is 3.96±0.14% and that of DTF substituted sensitizers has raised to 7.38±0.32 and 6.90±0.23%. The difference in PCE of CO, HDT-C1, and HDT-C2 is reflected in the IPCE spectra, as illustrated in Figure 4b. In case of CO sensitizer, it was observed maximum IPCE of ~60% at 410 nm. On the other hand, the introduction of donor DTF in HDT-C1 dye

IPCE rose to 78% and in case of HDT-C2 it further enhances to 80%. However, the presence of rhodanine-3-acetic acid anthoning group in HDT-C2 more broaden the IPCE spectra that will help in tapping more photons leads to high PCE than the remaining two dyes. But, this true only when compared to CO sensitizer and the reason might be due to its non-conjugated structure between rhodanine ring and carboxylic anchoring group whereas HDT-C1 sensitizer having cyanoacrylic acid anchoring group has maintained the conjugation.48 HDT-C1 dye with conjugated cyanoacrylic acid anchoring group not only enhances the electron injection into  $TiO_2$ conduction band but also slows the charge recombination as was the case in our previous reports. However, literature reports point out that the device efficiency drastically reduce the dyes having rhodanin-3-acetic acid when compared to cyanoacrylic acid group using same scaffold. In the present study the efficiency has not much reduced probably the charge regeneration is the same in both



Figure 4. (a) J-V characterstics (b) IPCE spectra of C0, HDT-C1 and HDT-C2 sensitizers.

The present DTF based D- $\pi$ -A dyes are showed better device performance over literature reported dyes in which the  $\pi$ -spacer is either triphenylamine or phenothiazine scaffold. There are many reasons for getting high efficiency of present dyes over literature reported ones in which the onset of the IPCE extends up to 650 nm and second one is that the present sensitizers HOMO level is very close to the oxidation potential of redox couple so that the driving force for the regeneration of oxidized dye is <0.2 eV.<sup>34,40,41,44</sup> On the other hand, the efficiency of **HDT-C1** and **HDT-C2** dyes lower that

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literature reported DTF-C3 (8.29%)<sup>38</sup> probably due to more extended  $\pi$ -conjugation so that the onset of IPCE extends up to 700 nm as a result in high efficiency. Further, the efficiency of **HDT-C1** and **HDT-C2** may enhance by the introduction more  $\pi$ -conjugation between carbazole  $\pi$ -spacer and anchoring group.

Table 2. Photovoltaic parameters of C0, HDT-C1 and HDT-C2 sensitizers.^e

Dyes	Voc (V)ª	Jsc (mA/cm²)⁵	FF°	ղ <sup>ժ</sup> <b>(%)</b>	Adsorbed amount of dye (mol.cm <sup>-2</sup> )
C0	0.76±0.02	7.22±0.37	0.72	3.96±0.14%	4.13 x 10 <sup>-7</sup>
HDT-C1	0.78±0.02	14.12±0.43	0.67	7.38±0.32%	4.06 x 10 <sup>-7</sup>
HDT-C2	0.76±0.03	13.19±0.46	0.69	6.90±0.23%	3.99 x 10⁻ <sup>7</sup>

<sup>a</sup>open-circuit photovoltage (Voc), <sup>b</sup>short-circuit photocurrent density (Jsc), 'fill factor (FF), <sup>d</sup>conversion efficiency ( $\eta$ ). <sup>e</sup>Errors were take an average of four photovoltaic devices.

### 3.4. Thermogravimetric Analysis

In addition about the efficiency of devices, the thermal properties of dyes are also essential for the commercialization of technology. For this reason, we have adopted thermogravimetric analysis (TGA) to understand the thermal stability of newly synthesized dyes. As reported in literature that the thiafulvalene derivatives thermal stability is high.<sup>49</sup> Figure 5 illustrates the TGA curves of sensitizers from 50 to 300°C at a heating rate 10°C min<sup>-1</sup> under an inert atmosphere. As seen in Figure 5, both **HDT-C1** and **HDT-C2** dyes are stable up to 150°C and the initial weight loss (~5%) observed 100 to 150°C is due to the removal of moisture. Among metal-free organic dyes, dithiafulvalene class of compounds are good thermal stability and also easy of synthesis; this allows one can think about its commercialization of technology.



Figure 5. TGA spectra of C0, HDT-C1 and HDT-C2 sensitizers with a heating rate 10°C min<sup>-1</sup> under N<sub>2</sub>.

### Conclusions

In conclusion, we have successfully introduced strong electron donor HDT unit into a carbazole for the first time to form HDT-

substituted carbazole (HDT-CBZ) hybrid donor using D-π-A-concept for application in DSSCs. Two novel sepsitizers9/bave:04been synthesized using HDT-CBZ donor in which either cyanoacrylic acid (HDT-C1) or rhodanine-3-acetic acid (HDT-C2) as acceptor or anchoring group. With the introduction of HDT donor, the absorption peak red-shifted and the PCE of DSSC was enhanced compared to simple carbazole sensitizer n of 3.96±0.14% (CO) to 7.38±0.32 (HDT-C1) and 6.90±0.23% (HDT-C2). The improved PCE might be attributed to the HDT moiety by improving the electrondonating capacity, decreasing dye aggregation, possible to increasing intramolecular charge transfer (ICT) from donor to acceptor. Also the driving force for the regeneration of oxidized dye from redox couple is <0.2 eV and retarding the charge recombination due to propeller structure of DTF moiety. These results are strongly representing that to change the molecular design approaches for DTF based DSSCs further careful manipulations and device fabrication would develop DTF sensitizers in this broad and rapidly rising area of metal-free DTF based organic sensitizers in photovoltaic applications.

## **Supporting Information**

Classification data of the compounds such as methods and instrumentation,<sup>1</sup>H NMR, ESI-MS and MALDI-MS spectra (**Figure S1-8**), fluorescence decay (**Figure S9**), theoretical and experimental UV-Visible spectra (**Figure S10**), Optimized and ESP structures of dyes (**Table S1**) and Comparison of the experimental optical properties with the theoretical data (**Table S2**) are available in supporting information.

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## "Hexyl dithiafulvalene (HDT)-substituted carbazole (CBZ) D-π-A based on JO4147E sensitizersfor dye-sensitized solar cells"

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We have successfully modified basic carbazole (CBZ) sensitizer (C0) by substituted anadditional excellent donor hexyl dithiafulvalene (HDT) at C6 position using D- $\pi$ -A concept inwhich either cyanoacrylic acid (HDT-C1) or rhodanine-3-acetic acid (HDT-C2) as acceptor oranchoring group for the applied to DSSCs. The PCE of DSSC was enhancedcompared to simple carbazole sensitizer (without HDT unit) 3.96% to 7.38%. Only few researcharticles are reported in metal-free DTF based organic sensitizers based DSSCs application until now, hence designs of diverse molecular structures pave the way for enhanced efficiency and urability of photovoltaic devices.

