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"Hexyl dithiafulvalene (HDT)-substituted carbazole (CBZ) D-π-A based sensitizers for dye-sensitized solar cells"

Naresh Duvva,^a Lingamallu Giribabu^{a,b*}

^aPolymers & Functional Materials Division, CSIR-Indian Institute of Chemical Technology,

Tarnaka, Hyderabad 500007, TS, India.

^bAcademy of Scientific and Innovation Research (AcSIR), Ghaziabad 201002, India.

giribabu@iict.res.in (ORCID: 0000-0001-5936-7729);

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1. Methods and Instrumentation

1.1. Absorption steady state and time resolved fluorescence measurements: The absorption spectrum was recorded on a Shimadzu (Model UV-3600) spectrophotometer at concentrations, 1×10^{-5} M. Spex model Fluorlog-3 used for Steady state fluorescence spectra for solutions having optical density at the wavelength of excitation (λ_{ex}) ≈ 0.15 . Time-resolved fluorescence measurements have been carried out using HORIBA Jobin Yvon spectrofluorometer. Briefly, the samples were excited at 386 nm and the emission was monitored at 395-750 nm, and count rates employed were typically 10^3 - 10^4 s⁻¹. DAS-6 software was used for the Deconvolution of the data, which was carried out by the method of iterative reconvolution of the instrument response function and the assumed decay function. Standard statistical tests employed to judge the goodness of the fit of the experimental data to the assumed decay function.

1.2. *Theoretical Calculations:* All of the optimized geometries for all the sensitizers were stable in their conformation by means of global minimum energy, which were carried out using the B3LYP hybrid functional(5)and 6-31(d,p) basis set as the input.^{1,2} Further calculations were done using Gaussian 09 (RevisionB.01) ab initio quantum chemical software on a personal computer.³ Ground state properties like energy-minimized structures and frontier molecular orbitals (FMOs) were implemented using Density Functional Theory (DFT) in the gas phase. Excited state properties like percentage of molecular contribution, oscillatory strength, and singlet transition energy were executed using Time Dependent Density Functional Theory (TDDFT) in tetrahydrofuran solvent. TDDFT calculations to describe the solvation of the dyes in tetrahydrofuran were carried out using the integral equation formalism polarizable continuum model (PCM) within the self-consistent reaction field (SCRF) theory.^{4, 5} Simulation of the major portions of the absorption spectra and interpretation of the nature of transactions were carried out by employing the software Gauss Sum 2.2.5.^{6, 7} The contributing percentages of individual units present in the dyes to the respective molecular orbitals were calculated

1.3. Device Fabrication and Photovoltaic measurements: we adopted from our previous reports for the preparation of TiO_2 photo electrodes (area: ca. 0.740 cm²) and Pt-coated

counter electrode. The procedure for the synthesis of the TiO₂ electrode and fabrication of the solar cells for the photovoltaic calculations were espoused previous procedures.^{8, 9} For the working electrode, the paste composed of transparent TiO₂ nano particle layer (~20 nm diameter) was screen printed on fluorine-doped tin oxide (FTO) conducting glass substrate (transmission >85% in the visible, sheet resistance 10 Ω /square). The required thickness (8µm) and cell area (0.25 cm²) was obtained by repetitive screen printing. Subsequently, an additional scattering layer made of anatase TiO₂ particles of 5µm thickness (~400 nm in diameter) was doctor blading on the active transparent layer to improve the device performance. Now the doctor blading layer sintered at 500°C for 1h. Surfcom 1400A surface profiler (Tokyo Seimitsu Co. Ltd.) was used to measure the thickness of the films. To coat the TiO_2 film, the dye was dissolved in THF solution at 0.2 mM concentration. To these dye dissolved solutions, the prepared TiO₂ films were immersed and kept at 25°C for 12 h, so dye was loaded on the TiO₂ films. The presence of water in the pores of TiO₂ causes reduced injection efficiency of the dye. Therefore, to avoid rehydration of the TiO2 surface or capillary condensation of water vapours from ambient air inside the film, the dye was coated immediately on to the TiO₂ after the high-temperature annealing. The electrode was dipped into the dye solution while it was still hot (80°C). After complete adsorption of the dye on TiO₂ surface photo electrode was removed from the solution, and the non-adsorbed dye was removed by washing with THF under a stream of dry air or argon. The Pt-counter electrode was prepared by the spin coating of H₂PtCl₆ solution onto FTO conducting glass substrate and heated to 385°C temperature for 15 min. The dye-coated TiO₂ film and thermally platinised FTO conducting glass counter electrode were separated by a Surlyn spacer (40 µm thick) and sealed by heating the polymer frame at 100°C. Finally, the DSSC cells were assembled by the electrolyte solution consisting of a mixture of 0.5 M LiI, 0.05 M I2, 0.5 M TBP, 0.5 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII) in acetonitrile solution. A black metal mask with an area of 0.25 cm² under A M 1.5 sunlight (100 mW cm⁻², WXS-155S-10: Wacom Denso Co. Japan) were used to measure the current-voltage characteristics. The incident photon-to-current conversion efficiency (IPCE) spectra were measured with a monochromatic incident light of 1 x 10¹⁶ photons cm⁻² in direct current mode (CEP-2000BX, Bunko-Keiki).



Fig. S1. ¹H NMR spectrum (400 MHz, CDCl₃) of compound (HDT-CBZ-CHO).



Fig. S2. MALDI-TOF spectrum of compound (HDT-CBZ-CHO).



Fig. S3. ¹*H* NMR spectrum (400 MHz, CD_2Cl_2) of compound (C0).



Fig. S4. ESI-MASS (m/z) spectrum of compound (C0).



Fig. S5. ¹H NMR spectrum (400 MHz, CDCl₃) of compound (HDT-Cl).



Fig. S6. MALDI-TOF spectrum of compound (HDT-C1).



Fig. S7. ¹H NMR spectrum (400 MHz, CDCl₃) of compound (HDT-C2).



Fig. S8. MALDI-TOF spectrum of compound (HDT-C2).



Fig. S9. Fluorescence decay ($\lambda ex = 380 \text{ nm}$, $\lambda em = 445 \text{ and } 495 \text{ nm}$) of C0, HDT-C1 and HDT-C2 in THF solution.



Fig. S10. Theoretical and Experimental UV-Visible spectra of (a) C0, (b) HDT-C1 and (c) HDT-C2 in THF solution.

Dye	Minimum energy in kcal/mol	Optimized structure	Electrostatic potential maps (ESP)
C0	0.8 x 10 ⁶	本がへ	
HDT-C1	2.14 x 10 ⁶		
HDT-C2	2.73 x 10 ⁶		

Table S1: The optimized structures and electrostatic potential maps (ESP) of C0, HDT-C1 and HDT-C2 sensitizers.

Table S2: Comparison of the experimental optical properties with the theoretical data by B3LYP in THF solvent.

Dye	^a λ _{max} (in nm)	^b λ _{max} (in nm)	^{c}f	^d E (eV)	% of Molecular Orbital Composition
C0	288, 320, 386	256, 279, 353	1.058	3.505	HOMO->LUMO (92%), H-2- >LUMO (3%)
HDT-C1	272, 379, 549	256, 306, 386	1.096	3.211	H-1->LUMO (19%), HOMO- >LUMO (71%), HOMO- >L+2 (7%)
HDT-C2	294, 430, 551	262, 300, 415	1.542	2.978	H-1->LUMO (41%), HOMO- >LUMO (52%), HOMO- >L+2 (3%)

^a Recorded absorbance in nm, ^b theoretical absorbance in nm, ^c Oscillation strength, and ^d excited state energy in eV.

References

- 1. D. A. Becke, J. Chem. Phys. 1993, 98, 5648–5652.
- 2. G. A. Peterson, MA. Al-Laham, J. Chem. Phys. 1991,94, 6081-6090.
- 3. M. J. Frisch, G. W. Trucks, H.B. Schlegel, G.E. Scuseria, et al. Gaussian **09**, Gaussian, Inc., Pittsburgh PA, 2009.
- 4. S. Miertus, E. Scrocco, J. Tomasi, Chem. Phys. 1981, 55, 117–129.
- 5. M. Cossi, V. Barone, R. Cammi, J.A. Tomasi, Chem. Phys. Lett. 1996, 255, 327–335.
- 6. N.M. O'Boyle, A.L. Tenderholt, K.M. Langner, J. Chem. 2008, 29, 839–845.
- R. Dennington, T. Keith, J. Millam, GaussView, version 5, Semichem Inc., Shawnee Mission KS, 2009.
- N. V. Krishna, J.V.S. Krishna, S.P. Singh, L. Giribabu, A. Islam, I. Bedja, J. Phys. Chem. C 2017, 121, 25691-25704.
- A. Islam, Md. Adktaruzzamn, T.H. Chowdhury, Ch. Qin, L. Han, I.M. Bedja, R. Stalder, K.S. Schanze, J.R. Reynolds, ACS Appl. Mater. Interfaces 2016, 8, 4616-4623.