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Rationalization of Excited State Energy Transfer in D-π-A Porphyrin Sensitizers Enhancing Efficiency in Dye-Sensitized Solar Cells

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Donor-π-Acceptor (D-π-A) porphyrin based photo-sensitizers are extensively utilized in dye sensitized solar cells (DSSCs). However, investigation on how the intramolecular photoinduced energy/electron transfer influences the device performance is still limited. Herein, we report three new D-π-A porphyrin sensitizers (LG8, LG9 and LG10) comprising of 3-ethynylfluoranthrene as the donor and 2,1,3-benzothiadiazole (BTD), 2, 3-diphenylquinoxaline (DPQ), and 2, 3-di thiophen-2-yl) quinoxaline (DTQ) auxiliary acceptors. The LG8 showed more efficient and red-shifted energy transfer between donor and acceptor which translates into a higher power conversion efficiency (PCE). UV−visible absorption and fluorescence spectra revealed a large bathochromic shift and a significant quenching of the donor emission confirming an efficient intramolecular energy transfer from the fluoranthene linked porphyrin to the auxiliary acceptor benzothiadiazole in LG8.

Density functional theory calculations showed that the LUMO of LG8 and LG10 destabilized and match with the conduction band edge of the anatase TiO2 nanoparticles. As a result, LG8 and LG10 are exhibiting the best power conversion efficiency (η = 3.0 %) compared to LG9 (η = 1.50 %) owing to faster electron injection from the dye excited states into the TiO2's conduction band. This work underlines that the modification of the electron donor and acceptor in D-π-A porphyrin sensitizers have noticeable influence on the photo-physical properties of π-conjugated systems thereby affecting device performances.

1. Introduction

The penetration of renewable energies to our energetic mix is indispensable owing to the excess consumption of fossil fuels and increased awareness of environmental consequences. In this context, solar energy received much attention amongst other green resources as enormous amount of sunlight can be converted to electricity. Recently, organic photocatalysts lead in high demand to generate flexible, stable and low production cost solar cells in which dye-sensitized solar cells (DSSCs) are of significant interest due to ease in fabrication, excellent incident photon-to-electron conversion efficiency (IPCE) while being eco-friendly. In 1991, Grätzel et al. introduced the basic principle mechanism of nanocrystalline DSSCs. In this technology, the core is the photosensitizer which rules the two key basic principle of PV, light harvesting, exciton formation and separation in contact with nanocrystalline TiO2 and a redox mediator in electrolyte. Earlier, ruthenium-based DSSCs exhibits certified PCE of over 11 %. However, low abundance of Ru metal, purification of isomers and lack of absorption into the NIR region prompts the development of new alternatives to further improve the stability, the efficiency and thus to accelerate DSSCs commercialization. Thereby, the development of metal-free organic dyes afforded to reach record PCEs exceeding 14 %.

Amongst all various photosensitizers developed, porphyrin dyes possess high molar extinction coefficients, broad absorption from visible to near-infrared (NIR) region and ease of structural modification at β- pyrrole and meso- positions to tune the optical and electrochemical properties. Initially, meso- phenyl carboxylic group at the pyrrole position, reaching a PCE of 7.1%. Subsequently, Grätzel et al. developed D-π-A porphyrin sensitizers by substituting the carboxylic group at the β-pyrrole position, achieving a PCE of 13%. Recently, we reported butterfly shaped D-π-A porphyrin systems comprised of phenothiazine as an electron donor and benzothiadiazole as an acceptors which result with the efficiency of 10.2 %. Furthermore, strong electron donating nature of phenanthroimidazole
substituted in porphyrin D-π-A systems achieved the efficiency of 8.2% upon co-sensitisation with an organic dye. However, device efficiency increase, induced by energy or electron transfer with the modifications of the electron and acceptor moieties in porphyrin D-π-A systems for DSSCs, has well documented in the literature. Therefore, we herein report a systematic investigation of fluoroanthene as an energy donor and various auxiliary acceptor units such as benzothiadiazole/quinoxalines attached to the meso-position of porphyrins (LG8-LG10) and studied their optical, electrochemical properties and device properties. Detailed studies revealed that intramolecular energy transfer is more favoured in the case of LG8 leading to higher efficiency compared to LG9 and LG10. These results suggest that the energy level matching between electron donor and acceptor units affects the device performance and leads towards design of diverse D-π-A systems for electronic and energy related applications.

Three porphyrin D-π-A sensitizers (LG8-LG10) are herein designed, comprising a fluoroanthene as an electron donor unit tethered to porphyrin in its meso-position and three different auxiliary acceptor groups: benzothiadiazole (BTD) for LG8, 2,3-diphenylquinoxaline (DPQ) for LG9 and 2,3-di(thiophen-2-yl) quinoxaline (DTQ) for LG10, all of three ending with a benzoic acid anchoring group. Fluoroanthene is considered as one of the good energy donating unit which absorbs in UV region, where energy separation and thus the device efficiency (Scheme 1). The detailed synthesis, characterization, energy transfer and device studies are herein presented and discussed.

3-bromofluoroanthene was used as received from Aldrich. 3-ethylfluoroanthene (1), 4-(7-bromobenzoyl)[1,2,5]thiadiazol-4-yl)benzoic acid (a), 4-(8-bromo-2,3-diphenylquinolinol-5-yl)benzoic acid (b), and 4-(8-bromo-2,3-di(thiophen-2-yl)quinolinol-5-yl)benzoic acid (c) 5-bromo-15-(Trisopropysilyl)ethyl-10,20-bis[2,6-di-octoxy phenyl]porphyrinato] Zinc(ii) (2) 4-(7-bromobenzoyl)[1,2,5]thiadiazol-4-yl)benzaldehyde were synthesized as reported in literature.

3-ethylfluoroanthene: 3-iodofluoroanthene was dissolved in piperidine (15 mL) and THF (15 mL) followed by addition of Pd(PPh3)2Cl2 (61.7 mg, 0.08 mmol), Trimethylsilylethylacetylene (TMSA) (0.37 mL, 2.64 mmol), Cul (16 mg, 0.08 mmol), PPh3 (23.08 mg, 0.08 mmol) and refluxed for 2 hours. The reaction mixture was brought to room-temperature while stirring and completion of the reaction was monitored by TLC. The solvent was removed by rotary evaporation. The residue was purified by column chromatography (EtOAc/n-hexane = 1/10) to give compound 1. HRMS (APPITOFM) m/z [M+H]+ calcd. for C46H22SiN8Zn, 866.29; found 866.30. 1H NMR (300 MHz, CDCl3) δ 8.32 (1H, d, J = 8.3), 7.91 (1H, d, J = 7.6), 7.85 (4H, m, J = 7.3), 7.52 (1H, t, J = 6.4), 4.38 (2H, t), 3.52 (1H, s).

3-[ethylfluoroanthene-15-(Trisopropysilyl)ethyl]-10,20-bis[2,6-di-octoxy phenyl]porphyrinato] Zinc(ii) (3): Compound 2 (270 mg, 0.196 mmol) and compound 1 (89.6 mg, 0.393 mmol) were dissolved in 30 mL of THF and 5 mL of triethylamine. To this Pd(PPh3)2Cl2 (11.3 mg, 0.010 mmol) and Cul (1.8 mg, 0.010 mmol) were added under an inert atmosphere. The reaction mixture was stirred at 40 °C for 24 hours. The completion of the reaction was monitored by TLC. The solvent was removed by rotary evaporation. The residue was purified by column chromatography (THF/n-hexane = 1/10) to give compound 3 (yield 59%) as a brownish green solid. MALDI-TOF: m/z [M+H]+ calcd. for C53H32F22N8O4SiZn, 1443.37; found 1444. 1H NMR (500 MHz, CDCl3), pyridine-d5) δ 8.92 (2H, d, J = 4.5), 9.65 (2H, J = 4.4), 8.93 (2H, d, J = 4.5), 8.87 (2H, d, J = 4.5), 8.80 (1H, d, J = 8.2), 8.33 (1H, d, J = 7.1), 8.08 (1H, d, J = 7.0), 8.03 (1H, d, J = 6.7), 7.90 – 7.85 (4H, m), 7.69 (3H, t, J = 8.5), 7.31 – 7.29 (2H, m), 7.00 (2H, d, J = 6.7), 3.86 (8H, t, J = 8.0), 2.20 – 2.15 (3H, s), 1.54 – 1.50 (16H, m), 1.43 (8H, s), 0.97 (12H, s), 0.77 (12H, d, J = 7.4), 0.57 (4H, s), 0.51 (4H, s), 0.45 (14H, J = 4.8), 0.41 (8H, s). FT-IR (neat, cm−1): 3446, 2923, 2856, 2130, 1633, 1585, 1453, 1379, 1334, 1249, 1234, 1203, 1159, 1094, 997, 882, 830, 783, 766, 711, 662, 467.

5,15-bis[2,6-dioctoxyphenyl]-10-(3-ethylfluoroanthene)-20-(4-(7-benzoyl)[1,2,5]thiadiazol-4-yl)carboxyphenylethynyl]porphyrinato] Zinc(ii) (LG8): To a solution of compound 3 (200 mg, 0.138 mmol) in anhydrous THF (20 mL) was added TBAF (0.6 mL, 1M in THF). The solution was stirred at 0 °C for 30 minutes under N2 atmosphere. The mixture was quenched with H2O and then extracted with CH2Cl2. The organic layer was dried over anhydrous Na2SO4 and the solvent was removed under reduced pressure. The residue (180 mg, 0.393 mmol) and compound 3 (200 mg, 0.138 mmol) in anhydrous THF were dissolved in a mixture of anhydrous THF (20 mL) and Et3N (8 mL) under nitrogen atmosphere, then Pd2(dba)2 (6.4 mg, 0.007 mmol) and AsPh3 (2.1 mg, 0.007 mmol) were added to the mixture. The solution was refluxed for 17 hours. The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (CH2Cl2/MeOH = 20/1), recrystallization from MeOH/Ether/To give dye LG8 (yield 59%) as a brownish green solid. Anal.Calcd. For C53H32F22N8O4SiZn % (1541.30): C, 75.59; H, 6.41;
MALDI-TOF: m/z [M-H]+calcd. for C$_{24}$H$_{44}$O$_{19}$N$_{8}$Zn % 1687.46; found, 1687. H NMR (300 MHz, CDCl$_3$/MeOH = 20:1, v/v), recrystallized from MeOH/Ether to give dye LG9 (yield 57 %) as a green solid. Anal. Calcd. For C$_{24}$H$_{44}$O$_{19}$N$_{8}$Zn: C, 79.01; H, 6.17; N, 4.94; O, 6.18; S, 2.04; Zn, 4.18. MALDI-TOF: m/z [M-H]+calcd. for C$_{24}$H$_{44}$O$_{19}$N$_{8}$Zn % 1687.46; found, 1687. 1H NMR spectra were obtained at 400 MHz using Bruker 400. Advanced NMR spectrometer with X-WIN NMR software and all the 1H NMRs were referenced by Trimethylsilane (TMS). Elemental, Vario MICRO CUBE analyzer was used to perform the elemental analysis. Electrochemical studies were performed on a PC-controlled CH instruments model CHI 620C electrochemical analyzer. 1 mM solutions in THF solvent were used for cyclic and differential pulse voltammetry studies. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate (TBAP) at scan rate of 100 mV/s using glassy carbon, saturated calomel electrode (SCE), platinum wire as working, reference and auxiliary electrode, respectively. A first cyclic voltammogram (CV) was recorded, and then ferrocene was added before the measurement of a second cyclic voltammogram to well determine the potential of both HOMO and LUMO levels. Spectro-electrochemical experiments were performed using CH instruments model CHI 620C electrochemical analyzer utilizing a three-electrode configuration of thin layer quartz spectro-electrochemical cell at 25 °C. The working electrode was a Pt gauze, Pt wire counter electrode and SCE reference electrode separated from the solution by a double bridge. Thermogravimetric measurements were carried out on Mettler Toledo TGA/DSC 851e instrument heating rate at 10 °C min$^{-1}$ with 10 mg of sample.  

### Steady-state absorption and time-resolved fluorescence measurements

The optical absorption spectra were recorded on a Shimadzu (Model UV-3600) spectrophotometer using concentration of solutions 1 × 10$^{-6}$ M for Soret band and 1 × 10$^{-5}$ M for Q band in THF solvent. Steady-state fluorescence spectra were recorded (Spex model Fluorolog-3) for solutions having an optical density of ca. 0.2 at the excitation wavelength. Excitation-emission map and time-correlated single photon counting (TCSPC) experiments were carried out using an Edinburgh Instrument FLS980 spectrometer. For steady-state, the setup is composed of a continuous Xe light source associated with double excitation/emission monochromators. TCSPC experiments were carried out using a 70 ps pulse width laser diode at 480 nm as an excitation source (20 MHz repetition rate, 50 pJ/cm$^2$ average energy, instrumental response of 90 ps FWHM) and a microchannel plate photomultiplier tube (MCP-PMT) Hamamatsu detector set after the first emission monochromator. A 510 nm long-pass filter was used in emission to reject light scattering from the glass. The numerical analysis of the excited-state lifetime has been determined after deconvolution of the photoluminescence decay considering the instrumental response function (IRF) determined using Ludox solution.

### DSSC device fabrication

Unless specified, all devices were fabricated with a standard mesoporous 8 µm thick TiO$_2$ films sensitized with either LG8, LG9 or LG10 dye in tert-butanol:acetonitrile (1:1 in volume) solvent mixture, including an optimized concentration of 2 mM of chenochoxycholic acid (CDCA) to avoid formation of molecular aggregation in both solution and at the surface of the nanocrystals. TiO$_2$ paste is commercial (Greatcell solar materials 18 NRT) Optimized electrolyte composition is based on high volatile acetonitrile solvent including 0.6 M of 1,3 dimethylimidazolium
iodide (DMII), 0.05 M of iodine, 0.1 M of LiI and 0.5 M of tert-butyl pyridine (TBP).

Picosccond Transient Absorption Spectroscopy (TAS) measurements

The picosecond pump-probe set-up for TAS measurements with a streak camera detector was used to investigate recombination kinetics and geminate recombination kinetics in the LG8-LG10 based DSSCs. The set-up is explained in details in our previous report.42 Dye regeneration and recombination kinetics are measured after pump excitation at 430 nm. A 700 µJ/cm² pump fluence was used. 455 nm long-pass filter (Thorlabs) was placed before the spectrophotograph to remove scattered light from the pump. The transient absorption is calculated from four streak images according to the equation:

\[ \Delta A = \log\frac{(\text{data - emission})}{(\text{monitor - dark})} \]

where data is the density of the image obtained when both pump and probe are on, emission when only pump is on, monitor when only probe is on, and dark when both pump and probe are off in order to subtract the contribution of the stray light. Each of these four images consisted of N integrated camera images. Measurements are performed in sequence: data, emission, monitor, dark and this sequence is repeated M times. In order to obtained satisfactory signal-to-noise ratio N was 500 and M = 5-10.

DFT studies

The attained optimized structures for LG8-LG10 were stable and confirmed by means of genuine global minimum energy, which was carried out by Density Functional Theory (DFT) and B3LYP hybrid functional43-31G(d,p) basis set43 were used as input for further calculations. All the calculations were carried out by Gaussian 09 package on personal computer.44 Energy-minimized structures, frontier molecular orbitals (FMOs) were executed ground state properties processed by Density Functional Theory (DFT) in the gas phase. The excited state properties, like the percentage of molecular contribution, oscillatory strength, singlet transition energy were investigated by employing the Time-Dependent Density Functional Theory (TD-DFT) in THF. The optimized geometries were used to determine the frontier molecular orbitals (FMOs) and subjected to single-point TD-DFT studies (first 20 vertical singlet-singlet transitions) to obtain the UV-Vis spectra of these dyes. MO6-2x function and the solvation of the dyes in tetrahydrofuran were described by the integral equation formalism polarizable continuum model (PCM)45,46 within the self-consistent reaction field (SCRF) theory in the TD-DFT calculations. To interpret the nature of electron transitions, foremost portions of the absorption spectra were simulated by GaussSum 2.2.5 software.47,48 The percentage contribution of individual moieties present in the dyes were calculated by their respective molecular orbitals.

3. Results and discussion

Synthesis

Scheme 2 illustrates the synthesis of new porphyrin dyes LG8-LG10 using Sonogashira coupling reactions. The precursors of three sensitizers i.e., TIPS derivate (3) were synthesized from compound 1 and 2 in the presence of Pd(PPh3)4 catalyst. Subsequently, deprotection of TIPS-acetylene of 3 treated with bromoaromatic acids (a-c) using AsPh3 and Pd(dba)2 followed by column chromatography results the LG8-LG10 sensitizers. All these sensitizers are characterized by spectroscopic techniques such as 1H NMR, MALDI-TOF-MS and FT-IR. Further, optical and electrochemical properties of LG8-LG10 were recorded using UV-visible absorption, transient absorption, fluorescence and cyclic voltammetry. These results suggest that the modification of the acceptor unit in D-π-A porphyrin sensitizers affects on energy levels of D-A linear π-conjugated systems and promote energy transfer from fluoranthene-linked porphyrin to auxiliary acceptor BTD, thus improving solar-to-electrical power conversion efficiency. Preliminary characterizations of all three sensitizers were carried out by elemental analysis, MALDI-MS, 1H NMR and FT-IR spectrosopies (see experimental and Figures S1 to S10).

Optical properties

To examine the ground-state electronic properties of fluoranthene and BTD, DPQ, DTQ comprised linear D-π-A porphyrin sensitizers LG8–LG10, UV-visible optical absorption spectra are recorded in tetrahydrofuran (THF) at a concentration of 1 × 10⁻⁵ M at 25°C. The two absorption bands at 400–500 nm and 600–750 nm of the LG8 are attributed to the Soret and the Q-band, respectively (Figure 1), whereas LG9 and LG10 exhibits similar spectral features (Figure S11). However, the Q-band of LG8 at 687 nm showed significant red-shift when compared to LG9 (643 nm) and LG10 (683 nm). It reveals that the incorporation of the benzo[c][1,2,5]thiadiazole (BTD) moiety in auxiliary position influenced on the ground state vibrational transitions responsible for this bathochromic shift in LG8 absorption maxima.49 Subsequently, calculated absorption maxima

![Scheme 2 Synthetic route for the LG8-LG10 dyes.](Image)

![Figure 1 Absorption (left, solid line) and emission (right, dashed line) spectra of porphyrin sensitizer LG8 in the THF solvent. Simulated absorption bands are shown as vertical bars.](Image)
DCB and coordinating solvent THF, at studies measured in non-coordinating solvents such as DCM and O-transfer process between donor and acceptor in Photo-induced intramolecular excited state energy/electron Emission studies in solution

Emission studies in solution

Photo-induced intramolecular excited state energy/electron transfer process between donor and acceptor in D-π-A porphyrin sensitizers LG8-LG10 is characterized by steady-state emission studies measured in non-coordinating solvents such as DCM and O-DCB and coordinating solvent THF, at λ\text{exc} = 358 nm where donor fluoranthene absorbs predominantly and compared with the emission of the individual constituent 3-ethynylfluoranthene (FLU). The emission intensity of donor fluoranthene is quenched relative to pristine compound 3-ethynylfluoranthene at room-temperature. Interestingly, the emission of fluoranthene overlaps with the absorption of the porphyrin π-spacer in D-π-A sensitizers as showed in Fig 1 & Fig 2. In addition, the appearance of porphyrin emission at ca.700 nm region suggests that the quenching of FLU emission intensity is due to intramolecular excitational energy transfer from singlet state of FLU to porphyrin. Furthermore, the excitation spectrum of the three sensitizers at the porphyrin emission maximum of 680 nm showed characteristic fluoranthene absorption bands suggesting the evidence of intramolecular excited energy transfer in D-π-A sensitizers. In addition, upon excitation at ca. 470 nm, where the porphyrin π-spacer absorbs predominantly and respective emission maxima with quantum yields are presented in Table 1. The emission maxima of all three sensitizers are bathochromic shifted that indicates excited state is more polar than the ground state such as BTD and thiophene units as π-spacer.49

Emission studies in solution

Fig. 2 Emission spectra of equi-absorbing solutions of donor, ZnTPP, LG8-LG10 in THF solvent at 358 nm.

at ca.700 nm region suggests that the quenching of FLU emission intensity is due to intramolecular excitational energy transfer from singlet state of FLU to porphyrin. Furthermore, the excitation spectrum of the three sensitizers at the porphyrin emission maximum of 680 nm showed characteristic fluoranthene absorption bands suggesting the evidence of intramolecular excited energy transfer in D-π-A sensitizers. In addition, upon excitation at ca. 470 nm, where the porphyrin π-spacer absorbs predominantly and respective emission maxima with quantum yields are presented in Table 1. The emission maxima of all three sensitizers are bathochromically shifted when compared to its pristine compound 3-ethynylfluoranthene at room-temperature.

Table 1. The emission maxima of all three sensitizers are included to support the changes in experimental absorption data via modifications of auxiliary acceptors in fluoranthene appended D-π-A porphyrin sensitizers as shown in Table 1. In addition, presence of heteroaromatic units in D-π-A systems are bathochromically shifted that indicates excited state is more polar than the ground state such as BTD and thiophene units as π-spacer.49

Fig. 3 a) Emission spectra of equi-absorbing solutions of ZnTPP and LG8-LG10 dyes in THF solvent.

yield data presented in Table 1. As a result, one can expect higher power conversion efficiency for LG8 sensitizer.

Time-Correlated Single Photon Counting (TCSPC) experiments were carried out in solution to determine the dynamic of the excited-state in solution for LG8-LG10 (Fig. 4). Regardless of the dye, the photoluminescence (PL) decay shows a single component feature. The excited states lifetime is faster for LG8 (τ = 1.20 ns) bearing the benzothiadazole compared to the quinoxaline-based LG9 (τ = 1.52 ns) and LG10 (τ = 1.48 ns), which for the latter the excited states lifetime is very similar. We have determined singlet state energies (bandgap, E\text{0-0}) from the absorption and emission spectra, in the range of 1.78-1.90 eV. This is comparatively lower than Zn Por counterpart (2.05 eV). Finally, we measured absorption spectra of all three sensitizers when anchored onto a 6 μm thick TiO₂ layer.

The absorption spectra of all the three sensitizers are broadened with a red-shift in the maxima. This is due to molecular aggregation

Fig. 4 Comparison of PL decay using TCSPC technique at 480 nm excitation wavelength LG8-LG10 dyes in tert-butanol:acetonitrile mixture including 2mM of CDCA (solution O.D. = 0.5). Fit after reconvolution from the IRF is represented in plain line.
in the self-assembled monolayer and the electronic coupling of the dye anchoring group with the TiO₂ nanoparticles, respectively.

**Electrochemical studies**

Cyclic voltammetry is employed for the electrochemical analysis of the LGB-LG10 dyes as shown in Fig. 5a and the corresponding data are reported in Table 1. The ground state oxidation potential (E_{ox}) of LG8-LG10 were found at +1.05 V, +0.95 V and +1.03 V (vs NHE), respectively. The excited state oxidation potential (E_{ox}*) of LG8-LG10 is obtained from the following expression E_{ox}*(HOMO) = E_{ox} - E_0. The resulting values are -0.75 V, -0.95 V and -0.75 V (vs. NHE), respectively. However, LG8 and LG10 showed decrease in energy gap compared to LG9 which leads to a red-shifted absorption tail and the relatively positive E_{ox}* level suggests that BTD and DTQ moieties play a crucial role in LG8 and LG10. On the other hand, excited state oxidation potential of LG8-LG10 sensitizers showed more reductive values than the conduction band edge of TiO₂ (-0.57 V vs. NHE)[30] and the ground state oxidation potential is more positive than the redox potential of I₃⁻/+ (0.35 V vs. NHE), which will afford an efficient electron injection and dye regeneration in the complete devices (Fig. 5b).

**Spectro-electrochemical studies**

Spectro-electrochemical studies of LGB-LG10 were carried out at a controlled oxidation potential of +1.10 V vs. NHE to determine the optical fingerprint of the oxidized dye and its stability. From the evolution of the UV-vis absorption spectra of LGB (Fig. 6), upon oxidation it is observed a decrease in intensity of the absorption bands at 475 nm and 687 nm corresponding to the Soret and Q bands, respectively. This evolution is concomitant with the formation of a new band at 430 nm attributed to the dye radical cation. Three isobestic points at 444 nm, 543 nm and 735 nm were observed during this process. Likewise, LG9 and LG10 porphyrin sensitizer exhibits the same spectral features observed as in LGB (Figure S9). Therefore, a higher stability of the oxidized species of LG8-LG10 porphyrins than in Ru-sensitizer N719 under similar conditions aid to improve the performance of solar cells. [31]

**Theoretical studies**

Theoretical DFT and TD-DFT calculations with functional basis set of B3LYP/6-31G(d, p) were performed to find the matching between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of LG8-LG10 porphyrin sensitizers with the TiO₂ nanoparticles and liquid electrolytes thereby to avoid the charge recombination process in DSSCs. The ground state optimized structures of LG8-LG10 based DSSCs are exhibiting an efficient energy transfer, stable oxidation potentials and suitable HOMO-LUMO levels. LG8-LG10 based DSSCs are...
HOMO-2 and LUMO+2 electrons are present on donor and porphyrin core, respectively (Fig. 7). Later, excited-state transitions of LG8-LG10 were calculated using polarizable continuum model (PCM) in THF with M06-2X function using B3LYP/6-31G (d,p) basis set. The resulting calculated vertical excitation energies for singlet and oscillator strengths match with the experimental data. Therefore, the incorporation of electron-deficient auxiliary acceptor units adjacent to the phenyl group aid to delocalize the LUMO orbitals of the sensitizer and promote electron transfer from porphyrin moiety to the acceptor unit, thus facilitating light harvesting and charge separation to reach long-lived of the excited state. As a whole, the electron distribution of LUMO of LG8 is more concentrated on acceptor or anchoring group and one can expect better device efficiency, when compared to LG9 and LG10 sensitizers.

Device studies

Optical, electrochemical and theoretical studies suggested that fluoroanthene appended porphyrin sensitizers in LG8-LG10 are Fig. 8 shows the evolution of current density–voltage (J–V) characteristics of the devices under standard A.M. 1.5G irradiation conditions (100 mW/cm²). LG8 and LG10 are showing the highest

| Sensitizer | Absorption $\lambda_{\text{max}}$ (nm), log $\varepsilon$ (M⁻¹ cm⁻¹)a | Emission $\lambda_{\text{max}}$ (nm), (a)b | $\tau$, ns (A%)c | $E_{0-0}$ (eV)d | $E_{\text{OX}}$ (V)/NHEe | $E^*_{\text{OX}}$ (V)f |
|------------|-------------------------------------------------|-----------------------------------------------|-----------------|----------------|-----------------|----------------|
| LG8        | 475 636 687 (5.43) 458 702s (0.01) 0.25        | 1.20(100) 1.80 1.05 -0.75                     |
| LG9        | 464 578 643 (5.54) 459 660 (0.02) 0.19        | 1.52(100) 1.90 0.95 -0.95                     |
| LG10       | 473 645 685 (5.30) 458 698 (0.01) 0.24        | 1.48(100) 1.78 1.03 -0.75                     |

*Solvent: THF, Error limits: $\lambda_{\text{max}}$, ±1 nm, ε±10%. Error limits: $\lambda_{\text{max}}$, ±1 nm, ϕ±10%. Error limits: ±10%. Error limits: $E_{0-0}$ was determined from the intersection of absorption and emission spectra, Error limit ±10%. *Solvent: THF, error limits: $E_{\text{OX}}$, ±0.03 V, 0.1 M TBAP. * $E_{\text{OX}}$ was determined as $E_{\text{OX}} = E_{0-0}$. 

Fig. 7 Isodensity (0.02) plots of FMOs by using the B3LYP method 6-31G(d,p).
compared to benzothiadiazole (BTD) and 2, 3-di (thiophen-2-yl) quinoxaline (DTQ) in LG8 and LG10. The LUMO is more destabilized in LG9 dye and is almost similar for both LG8 and LG10 dyes. The photovoltaic characteristics are for LG8 ($J_{SC} = 7.8$ mA/cm$^2$, $V_{OC} = 0.58$ V, FF = 68.3 %), LG9 ($J_{SC} = 3.53$ mA/cm$^2$, $V_{OC} = 0.51$ V, FF = 72.0 %) and LG10 ($J_{SC} = 6.28$ mA/cm$^2$, $V_{OC} = 0.56$ V, FF = 73.0 %). Thus, the incorporation of auxiliary acceptors like BTD and heteroaromatic substituents on quinoxaline moieties affords to improve the dye performances compared to phenyl groups on quinoxaline unit.

IMVS/IMPS analysis show that changing the acceptor unit of the new porphyrin dyes affects both the non-geminate recombination (ie. interfacial electron transfer with the redox mediator) and the electron transport time (Fig. 9). Whereas benzothiadiazole and 2,3-di-thiophen-2-yl quinoxaline are providing very similar properties, the introduction of the 2,3 diphenylquinoxaline in LG9 dyes accelerates by ca. two times the non-geminate recombination and affects by a similar order the electron transport, signifying that charge collection efficiency in LG9 dye is lower than LG8 and LG10 counterpart. This provides a first explanation on why LG9 suffers from lower photovoltage and photocurrent density in full devices. These results stress that the shorter excited state lifetime of LG8 dye does not penalize the device performance.

Table 2: Photovoltaic performance parameters of LG8-LG10 sensitizers.

| Dye   | TBP (mM) | $J_{SC}$ (mA/cm$^2$)* | $V_{OC}$ (V) | FF (%) | η (%) |
|-------|----------|------------------------|--------------|--------|-------|
| LG8   | 0.5 M    | 7.8                    | 0.58         | 68.3   | 3.11  |
| LG9   | 0.5 M    | 3.53                   | 0.51         | 72     | 1.50  |
| LG10  | 0.5 M    | 6.28                   | 0.56         | 73     | 2.86  |

*Error limits: $J_{SC} = ±0.20$ mA cm$^{-2}$, $V_{OC} = ±0.30$ mV, and FF = ±0.03.

Kinetic studies

Fig. 9 Comparison of (a) electron lifetime and (b) transport time determined by IMVS and IMPS respectively for LG8-LG10-based DSSC.

Fig. 10 Comparison of transient absorption kinetic for LG8-LG10-based DSSC (a) including $I_3/I^-$ redox mediator in electrolyte, (b) without redox couple in electrolyte. The devices were pumped at 430 nm (10 Hz) with an energy of 700µJ/cm$^2$.

Transient absorption spectroscopy using a Streak camera in detection for both spectral and temporal resolution was employed to investigate LG8-LG10 dye regeneration and geminate recombination kinetics (Fig. S18). The transient dye radical cation absorption spectrum for the different dyes is presented in Figure S19 and the corresponding kinetic in Fig. 10.

Dye radical cations of all dyes show in a broad spectral range two bands, one at 550 - 620 nm and another at 750 - 800 nm. This is in a good agreement with the spectral evolution upon oxidation obtained by spectro-electrochemistry in TBAP/THF (Fig. 6). LG8-
LG10 dye radical cation formed after 30 ps pump at 430 nm depopulates within 1.5 μs in a process of dye regeneration where the transfer of an electron from the redox couple regenerates the original dye oxidation state. Unwanted and competitive process to the dye regeneration step is the back electron transfer from TiO₂ to the dye radical cation. Lifetime of this geminate recombination process is determined to be in the range of 60 μs, which is sufficiently longer than regeneration. Interestingly, both regeneration and non-geminate recombination are independent to the type of acceptor unit. This result combined with TD-DFT calculations confirm that these two kinetic processes are mainly governed by the fluoranthene unit attached to the porphyrin core. Based on these two numbers, one can estimate that the yield of dye regeneration is in the range of 97.5 %, thus suggesting that dye regeneration is not a limiting step in the device performance.

Finally, we have carried out thermogravimetric analysis of all three new sensitizers to characterize the dye’s thermal stability; a characteristic essential for commercialization of the technology. The thermal behaviour of three sensitizers suggests that these dyes are stable up to 200 °C and the initial weight loss in between 200 °C to 250 °C is due to decarboxylation of cyanoacrylic group (Fig S21). Therefore, these studies revealed that LG8-LG10 based porphyrin sensitizers highly thermal stable and these values are close to the analogous of previously reported porphyrin sensitizers.

Conclusions

In summary, the design of fluoranthene D-π-A based porphyrin sensitizers alter the photovoltaic performance upon varying the acceptor moieties such as benzothiadiazole (BTD), 2, 3-diphenylquinazoline (DPQ) and 2, 3-di (thiophen-2-yl) quinoxaline for LG8, LG9 and LG10, respectively. Optical properties suggest that the presence of BDT acceptor group in LG8 sensitizer shift the absorption maxima towards the red region. Emission, electrochemical and theoretical studies indicates efficient intramolecular excited energy transfer mechanism and the energy transfer efficiency is higher in LG8 than LG9 and LG10 sensitizers. Spectro-electrochemical studies revealed that the ease of oxidation in porphyrin to form radical cation at applied potential of +1.10 V vs. NHE in LG8. Furthermore, the DFT calculations supported the energy transfer mechanism while HOMO levels localized on porphyrin and fluoranthene while LUMO on the acceptor moieties. Device performance of LG8 exhibits PCE of 3.11% suggest that the novel design of diverse electron and acceptor moieties appended D-π-A planar system may find applications not only in DSSCs but also in broader perspectives for organic electronics.

Conflicts of interest

“There are no conflicts to declare”.

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