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Heterotriangulene-based unsymmetrical squaraine dyes: synergistic effects of donor moiety and out-of-plane branched alkyl chains on dye cell performance

Neeta Karjule^{†,‡}, Munavvar Fairoos MK[†] and Jayaraj Nithyanandhan^{*,†,‡}

Unsymmetrical squaraine sensitizers with two different donor moieties, triphenylamine (**NSQR**) and heterotriangulene (**NSQ1-3**), for dye-sensitized solar cell (DSSC) have been designed and synthesized. These dyes utilize the indolium moiety to control charge recombination dynamics at TiO₂-dye-electrolyte interface by connecting linear and branched alkyl functionalities. In the present study, an efficient heterotriangulene (HT) donor and branched alkyl group at sp³-C atom were strategically incorporated to increase the power conversion efficiency (PCE) of zwitterionic dyes by improving photo-current density (J_{sc}) and open-circuit potential (V_{oc}) of the cell. Among these four dyes, **NSQ3** exhibited the highest efficiency of 6.73% with a J_{sc} of 18.74 mA/cm², V_{oc} of 0.53 V, and fill factor (*ff*) of 68.3%, without any co-adsorbent under irradiance of 100 mW/cm² (simulated AM 1.5G sunlight). In presence of 3α , 7α -dihydroxy-5 β -cholanic acid (CDCA), **NSQ1**, **NSQ2** and **NSQ3** showed efficiency of 7.07%, 7.38% and 7.17%, respectively. Despite the low V_{oc} , far red light harvesting efficiency, reduced dye aggregation, long lifetime (τ) of injected electron and high quantum efficiency of **NSQ1-3** played constructive role to achieve high PCE efficiency. Deceleration of charge recombination for **NSQ** dye cells were further studied by electrochemical impedance spectroscopy (EIS) and open-circuit photo-voltage decay (OCVD) measurements.

1. INTRODUCTION

DSSCs have been considered as a promising alternative to conventional inorganic p-n junction silicon-based solar cells for solar energy-to-electricity conversion.^{1,2} Since the first report by O'Regan and Grätzel in 1991, dye cells have been received considerable attention because of their low fabrication cost and diversity in device components.³ Sensitizers used in dye cell to absorb the photons are broadly classified into two categories: 1) organometallic dyes (ruthenium-polypyridyl complexes^{4.5} and zinc porphyrin dyes)⁶ and 2) metal-free organic dyes^{2.8}. Particularly, to harness the long wavelength photons, near-infrared (NIR) light harvesting dyes like phthalocyanines,^{9,10} polymethines,¹¹ and porphyrins^{12,13} have been explored and so far the best conversion efficiency was obtained for porphyrin based dye (SM315) is 13% with Co(II)/(III) redox couple.¹⁴

Squaraines, one of the polymethine dyes, have attracted special interest because of their intense absorption in the farred and near-infrared (NIR) regions, $\frac{15,16,17}{10}$ and high molar absorptivity (~10⁵ M⁻¹ cm⁻¹) compared to zinc porphyrins.¹⁸ However, these zwitterionic molecules aggregate on metal oxide surface that reduces the excited state lifetime, and leads

to inefficient power conversion. $\frac{19,20}{2}$ There are two types of squaraine dyes known in the literature – symmetrical $\frac{21,22}{2}$ and unsymmetrical $\frac{23,24}{2}$, and the directionality of electron injection was realized better in the latter. The device efficiencies for symmetrical and unsymmetrical dyes have been reached at 6.18% (VG10-C2)²⁵ and 8.9% (DTS-CA)²⁶ respectively. Recently, few triphenylamine (TPA) based unsymmetrical squaraine dyes have been synthesized^{27,28} and the highest PCE of 6.29% was achieved for JK216 dye.²⁹ These sensitizers exhibited intense absorption bands in the NIR region $\frac{30}{2}$ but they tend to form either H- or J- type aggregates and reduce the excited state electron lifetime.³¹ Also the propeller shaped TPA lacks rigidity and poor extension of π -conjugation over the whole molecule due to the large dihedral angles between the phenyl rings and the plane of the N-bonded carbon atoms.^{32,33} Based on the understanding from the previous studies, planar heterotriangulene donor system was introduced in donor-πacceptor DSSCs to achieve fast electron injection,³⁴ increases the electronic coupling between donor and acceptor moieties of the dye, and localize the positive charge resulting after electron injection.³² By introducing a planar rigid moiety,³⁵ dyes tend to assemble via π - π stacking while anchoring on TiO₂ and to keep dyes separated for avoiding the aggregationinduced decay of the excited state, indolium moiety of the unsymmetrical squaraines was functionalized with in-plane and out-of-plane alkyl functionalities.³⁶

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[†] Physical and Materials Chemistry Division, CSIR-National Chemical Laboratory, CSIR-Network of Institutes for Solar Energy, Dr. Homi Bhaba Road, Pune, India-411008. *E-mail: j.nithyanandhan@ncl.res.in

^{*}Academy of Scientific and Innovative Research, New Delhi 110025, India. Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

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Figure 1. Molecular structures of the unsymmetrical squaraine NSQR and NSQ1-3 sensitizers.

In this study, we report a new dye design to improve the PCE of unsymmetrical squaraine by taking the advantage of a strong donor and an alkyl functionalized indolium unit (**Figure 1**). In both dyes, squaric acid unit is linked between either HT or TPA donor and indolium moiety having a carboxylic acid as an anchoring group. Introduction of long alkyl chains on indolium unit is expected to increase the solubility, decrease the undesirable dye aggregation and suppress dye desorption by reducing the infiltration of solvent to the TiO₂ surface.^{37,38} We systematically connected alkyl groups in the N- and sp³-C atoms of indolium unit to provide an in-plane and out-of-plane branching of hydrophobic chains, respectively.³⁹ Current-

voltage (*I-V*) measurements showed that HT based dyes (**NSQ1-3**) outperformed TPA based squaraine (**NSQR**) in terms of both J_{sc} and V_{oc} . Although, **NSQ2** and **NSQR** shows similar molecular structure apart from the different donors, it is found that, J_{sc} of **NSQ2** significantly increased by 41.2% than **NSQR** because of the effective conjugation. In-plane and out-of-plane alkyl groups of **NSQ3** further increased the J_{sc} by 30.2% and hence achieved the PCE of 6.73% without any co-adsorbent. Bulky, passivating indolium unit close to the anchoring group suppressed the charge recombination, and the V_{oc} of **NSQ3** increased by 118 mV without CDCA than **NSQR**, which has been verified by photo-voltage decay



Scheme 1. a) Syntheses of indolium iodide (3a-3c), b) NSQ 1-3 dyes and c) NSQR dye.

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2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization

The molecular structure of sensitizers and their synthetic scheme are illustrated in Figure 1 and Scheme 1, respectively. Synthesis of unsymmetrical squaraine sensitizers, NSQR and NSQ1-3, requires semi-squaraine and an indolium salt with either N- or sp³-C or both atoms functionalized with alkyl groups. To reduce the number of steps involved in the synthesis, we have chosen TPA and HT derived semi-squaric acid and suitably functionalized indolium salt as the precursors. For the indolium moiety contains sp³-C atom functionalized with alkyl groups, suitably substituted branched methyl ketone is required and we have chosen judiciously 3octyltridecan-2-one. The branched methyl ketone was synthesized starting from oxidation of branched alcohol to the corresponding aldehyde. Further reaction with MeMgI afforded the corresponding secondary alcohol which was oxidized to give the required precursor in moderate yield and reacted with 4-caboxyphenylhydrazine to provide the intermediate (2a-2b). The corresponding indolium salts (3a-3c) were synthesized by reacting with alkyl halide in moderate yield. The semi-squaraine derivatives 4c and 5c were prepared by reaction of 4a and 5a with squaryl chloride followed by acid hydrolysis of the semi-squaryl chloride derivatives.⁴² A condensation reaction between semi-squaryl chloride derivatives of 4c or 5c and 5-carboxy-2,3,3-trialkyl-1-alkylindolium units (3a-3c) afforded the NSQ sensitizers. All the sensitizers have good solubility in MeCN, CH₂Cl₂, CHCl₃, DMSO and limited solubility in MeOH. All the intermediates and final dye molecules were characterized by ¹H- and ¹³C- NMRs and mass spectrometry (HRMS-ESI).

2.2. Photophysical Properties

The UV-Vis absorption spectra of **NSQR** and **NSQ1-3** in CH₃CN solution, on transparent mesoporous TiO₂ film, and the emission properties are shown in **Figure 2** and summarized photo-physical properties are provided in **Table 1**. The absorption spectra of both **NSQR** and **NSQ1-3** were exhibited an intense absorption band centered around 643 nm and 674 nm, respectively, corresponding to internal charge transfer (ICT) transition, with a high molar absorption coefficient (ϵ) in the range of 10⁴ M⁻¹ cm⁻¹.

Apart from the ICT band, **NSQ1-3** shows π - π^* transition between 400-500 nm with lower ε values (~10³ M⁻¹ cm⁻¹). After substituting the propeller triphenylamine donor with planar triphenylamine, i.e. heterotriangulene, absorption maxima (λ_{max}) of **NSQ1-3** is red-shifted around 30 nm relative to that of **NSQR**, due to extended conjugation. The absorption spectra of **NSQ1-3** are broadened on TiO₂ thin film due to the interaction of carboxylic acid groups with the surface titanium ions and λ_{max} is blue shifted by 32 and 38 nm for **NSQ1** and **NSQ2**, respectively, because of H-type of aggregation.⁴³ However, **NSQ3** shows only 8 nm shift towards higher energy because of



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Figure 2. (a) Absorption (solid line) and emission (dot line) spectra of NSQ dyes in CH_3CN solution (b) Absorption spectra of NSQ sensitizers (0.1 mM in CH_3CN) adsorbed on the transparent TiO₂ film (6 μ m), dipped for 10 min.

the presence of out-of-plane alkyl segments on indolium sp³-C atom, which effectively suppresses dye aggregation. It is observed that emission λ_{max} of **NSQ** sensitizers are shifted to longer wavelength and maximum stokes shift of ~70 nm is observed for **NSQ1-3** sensitizers, which is relatively small for **NSQR** (~50 nm). This finding qualitatively supports the larger dipole moments in excited state for **NSQ1-3** in solution (**Figure 2a**) due to additional conjugation from HT unit.

2.3. Electrochemical Properties

Cyclic voltammetry measurements were carried out in CH₃CN to understand the feasibility of electron transfer from the excited state of the sensitizers to the conduction band of the TiO₂ and the regeneration of oxidized dyes by the electrolyte. Redox potentials of **NSQR** and **NSQ1-3** were measured (**Figure 3** and **Table 1**), and exhibited the quasi-reversible first ground-state oxidation potential of **NSQR** at 0.78 and for **NSQ1-3** at 0.79 (**NSQ1**), 0.81 (**NSQ2**) and 0.81 (**NSQ3**) V vs NHE. E_{ox} of NSQs was low enough to get regenerated by iodide (0.4 V vs NHE). Highest occupied molecular orbital (HOMO) of the **NSQR** was not affected after substituting with fused triarylamine, **NSQ1**, as listed in **Table 1**. The lowest unoccupied molecular orbital (LUMO) of **NSQ dyes** were calculated by subtracting E_{0-0} from E_{HOMO} and the values are found to be -1.08, -0.98, -0.95



Figure 3. (a) Cyclic voltammograms of **NSQR** and **NSQ1-3** measured in CH₃CN, with TBAClO₄ (0.1 M) at the scan rate of 50 mV s⁻¹ (b) Energy level diagram for the **NSQ** sensitizers vs NHE.

and -0.96 V vs NHE for **NSQR**, **NSQ1**, **NSQ2** and **NSQ3**, respectively, which lie above the conduction band edge (CB) of TiO₂ (-0.5 V vs NHE)⁴⁴ that allows an effective electron injection into the conduction band of TiO₂ as shown in **Figure 3b**. **NSQR** and **NSQ1-3** showed a band gap (E_g) in the range of 1.7-1.9 eV, which are in good accordance to the band gaps determined from the DFT studies.

2.4. Theoretical Investigations

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The molecular geometries of NSQ sensitizers were optimized using density functional theory (DFT) at B3LYP/6-31G^{**} level with the Gaussian 09 program⁴⁵ and the isosurface plot for HOMO-1, HOMO, LUMO, and LUMO+1 are shown in **Figure 4**



Figure 4. HOMO and LUMO isosurface plots for NSQR (left) and NSQ2 (right), respectively.

(NSQR, NSQ2) and **Figure S47**. In **NSQ1-3** sensitizers, the electron density in HOMO and HOMO-1 was more delocalized on donor part than **NSQR** and also well distributed throughout squaric acid, whereas the LUMO was delocalized towards indolium unit contains electron withdrawing carboxylic acid. This HOMO and LUMO overlap facilitates the effective charge transfer from donor to anchoring unit and hence shows a red-shifted λ_{max} in the absorption spectrum. The LUMO+1 for all sensitizers were mainly located near to anchoring group. On the other hand, in **NSQR** the HOMO-1 was located on squaric acid unit, which indicates the inability of triarylamine to regenerate the dye after injection of electron to TiO₂ compared to other NSQ dyes. These overall DFT results

Table 1. Photophysical and electrochemical properties of squaraine dyes										
SQ Dyes	λ _{max} /CH ₃ CN (nm) ^a	λ _{max} /TiO ₂ (nm)	λ _{max /em} (nm)	ε×10 -1 -1 a (M cm)	E _{g/DFT} (eV)	E _{ox/onset} (V vs Ag/Ag ⁺)	Ε _{ΗΟΜΟ} (V vs NHE) ^c	E ₀₋₀ (eV) ^d	E _{LUMO} (V vs NHE) ^e	
NSQR	643	624	696	5.5	2.13	0.28	0.78	1.86	-1.08	
NSQ1	673, 458	641	746	6.1, 0.86	2	0.29	0.79	1.77	-0.98	
NSQ2	674, 464	636	746	6.9, 0.73	2.01	0.31	0.81	1.76	-0.95	
NSQ3	674, 464	666	743	6.5, 0.92	2.01	0.31	0.81	1.77	-0.96	

^aAbsorption and emission spectra, molar extinction coefficients (ϵ) were measured in CH₃CN. ^bOn 6 µm transparent TiO₂ film. ^cThe oxidation potentials were measured in CH₃CN solutions with tetrabutylammonium perchlorate (TBACIO₄) as supporting electrolyte, ferrocene/ferrocenium (Fc/Fc⁺) as an internal reference and converted to NHE by addition of 0.63 V. ^dOptical energy gaps (E₀₋₀) were deduced from the intersection of absorption and emission spectra, E_{0-0} (eV) = 1240/ λ . ^e E_{LUMO} was calculated from E_{LUMO} (V vs NHE) = E_{HOMO} (V vs NHE) - E_{0-0} .



Figure 5. Selected dihedral angles of NSQR and NSQ3 calculated from the optimized ground state geometry using density functional theory (DFT) at B3LYP/6-31G** level with the Gaussian 09 program (hydrogen atoms are removed for better clarity).

suggest that the HOMO-LUMO or HOMO-LUMO+1 excitations can afford electron flow from the donor unit to the anchoring group.

Degree of conjugation between donor and acceptor could be influenced by dihedral angle between benzene and nitrogen atom of TPA or HT donor (θ_1), donor and squaric acid unit (θ_2), and squaric acid and indolium unit θ_3 .⁴⁶ θ_1 for **NSQR** is found to be more deviated than NSQ1-3 dyes, indicates a better co-planarity of donor-acceptor parts (Figure 5). The θ_1 value of NSQR is 47.06°, whereas for NSQ1-3 it is close to 0° (Table S1). Bulky alkyl functionalities of indolium unit exhibits extended conformation with θ_4 of 176.6°, which helps to improve the photo-physical properties by reducing the aggregation as well as extending the conjugation. Distance between (i) sp^{3} -C (methylene group of HT) to -O atom of carboxylic acid, (ii) terminal carbon atoms of sp³ -branched alkyl chain and (iii) sp³-C (indoline) to –O atom of carboxylic acid were 19.6 Å, 23.1 Å, and 6.2 Å, respectively for NSQ3 (Figure S48). Such structural features may lead to better exposed HOMO for efficient dye regeneration, reduced dye aggregation and charge recombination due to extended conformation of alkyl groups, and the presence of long branched hydrophobic alkyl chains near to the surface, respectively.

2.5. Photovoltaic Performance of DSSCs

Incident photon-to-current conversion efficiency (IPCE) of **NSQR** and **NSQ1-3** DSSCs are shown in **Figure 6b** and **7b**. The increased J_{sc} value of **NSQ1-3** sensitizers are reflected in the IPCE spectra, and shows broader and higher IPCE in the range of 400 to 800 nm, reaching a maximum of 73% and 69% at 420 and 635 nm, respectively, in the absence of CDCA for **NSQ3**. **NSQ3** dye converted 50% of the photons at 750 nm, whereas **NSQR** shows only 8% IPCE response at the same wavelength. NIR photons are effectively converted when the TiO₂ sensitized with **NSQ3** than any other dyes in the series without CDCA, with the IPCE of 30% at 780 nm, where **NSQ1** and **NSQ2** shows below 10%. After the addition of CDCA, NSQs shows further increase in IPCE at higher wavelength region, and at 750 nm **NSQ1**, **NSQ2** and **NSQ3** exhibits IPCE of 50%, 58% and 62%,

respectively. But for **NSQR**, IPCE response around 750 nm is 15% at the same condition.

The current density–voltage (*J–V*) characteristics of DSSCs based on **NSQR** and **NSQ1-3** were evaluated under simulated AM 1.5G solar light (100 mW cm⁻²), and the curves are shown in **Figure 6a** and **7a**. In the case of **NSQR**, **NSQ1** and **NSQ2**, the moderate performance is achieved without any co-absorbent, because of the aggregation of dyes in the absence of CDCA. Among the NSQs, **NSQ3** sensitized cells gives better performance without CDCA and achieved an overall power conversion efficiency (η) of 6.73% with a J_{sc} of 18.74 mA cm⁻² and V_{oc} of 0.53 V. In particular, among the four dyes the **NSQ3**



Figure 6. (a) *J*–*V* curve and (b) IPCE spectrum of NSQR, and NSQ1-3 sensitizers without co-adsorbent (CDCA).

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Figure 7. (a) *J*–*V* curve and (b) IPCE spectra of NSQR, and NSQ1-3 in the presence of CDCA.

shows the maximum V_{oc} of 0.54 V and 0.53 V with and without CDCA, respectively, proving the strong ability of branched and long alkyl side chain on chromophore that prevents surface aggregation and reduces the charge recombination even without any co-adsorbent.⁴⁷

are shown in **Figure S49** and photovoltaic performances are summarized in **Table 2**. As expected, the addition of CDCA has a positive impact on improving the V_{oc} and J_{sc} values of NSQ sensitizers based DSSCs, and hence after the addition of 10 equivalents of CDCA, the **NSQ2** sensitized cells shows an overall power conversion efficiency (η) of 7.4% with a J_{sc} of 20.57 mA cm⁻², V_{oc} of 0.53 V and *ff* of 0.68, while triphenylamine based **NSQR** sensitized cells were exhibited a relatively poor performance with an overall η of 4.63% at the same amount of co-adsorbent due to lower J_{sc} (14.95 mA cm⁻²) and V_{oc} (0.47 V) values. The **NSQ1** sensitized cell was achieved a J_{sc} value of 21.32 mA cm⁻², V_{oc} of 0.49 V, and *ff* of 0.68, corresponding to η of 7.07%. Device made with **NSQ3** reached at a J_{sc} of 20.11 mA cm⁻², V_{oc} of 0.54 V, *ff* of 0.66 and overall conversion efficiency of 7.17% with the addition of minimum

Results of five cells with deviation for optimized dye/ CDCA

amount of CDCA (1 equivalent), and the curves are shown in Figure 7a. It is found that the J_{sc} and V_{oc} of NSQ3 dyes decreases with further addition of CDCA due to competitive binding of CDCA over dyes. These results indicate that the addition of large amount of CDCA is not beneficial for NSQ3 to enhance the photovoltaic performance (Table S2 in SI). Dye desorption results indicate the modulated adsorption of dyes on TiO₂ with respect to their structure (Table 2 and Figure S50). Dye loading ability decreases in the order of NSQR > NSQ1 > NSQ2 ≈ NSQ3, due to progressive increase of alkyl groups near TiO₂ surface which blocks the dye anchoring to the pentacoordinated Ti center. However, addition of 10 equivalents of CDCA abruptly changes the quantity of adsorbed dyes in the case of NSQ3 over other three dyes that leads to decreased device efficiency (Table S2). All the dyes with HT donor showed high J_{sc} with and without CDCA than triphenylamine donor. Herein, considering the very similar configuration between NSQ1-3 and NSQR, the incorporated HT donor and branching at chromophore paved the way to extend the light harvesting ability and reducing the charge recombination property. The distinct enhancement of J_{sc} and

Table 2. Photovoltaic parameters for NSQ1-3 and NSQR with and without co-adsorbent. ^a										
NSQ Dye Cell	V _{oc} [V]	J _{sc} [mA/cm ²]	ff [%]	η[%]	Amount of adsorbed dyes (×10 ⁻⁷ mol cm ⁻²) ^b					
NSQR	0.406±0.002	7.4±0.29	66.8±0.8	2.01±0.11	2.12					
NSQR/CDCA (1:10)	0.467±0.004	14.64±0.31	64.4±1.3	4.40±0.23	1.56					
NSQ1	0.465±0.004	11.93±0.38	68.7±0.5	3.81±0.18	1.81					
NSQ1/CDCA (1:10)	0.486±0.002	20.77±0.55	67.6±0.4	6.82±0.25	1.01					
NSQ2	0.474±0.002	12.90±0.18	65.1±1.0	3.98 ±0.13	1.23					
NSQ2/CDCA (1:10)	0.526±0.001	20.35±0.22	66.9±1.2	7.16±0.22	0.87					
NSQ3	0.521±0.004	18.38±0.36	68.1±0.20	6.53±0.20	1.13					
NSQ3/CDCA (1:1)	0.540±0.001	20±0.11	65.7±0.25	7.09±0.08	0.94					

^aPhotovoltaic performance of **NSQR** and **NSQ1-3** with deviation of 5 cells, thickness of electrode: 8+4 μ m (transparent+ scattering) layer of TiO₂, Electrolyte: 0.5 M DMII, 0.1 M Lil, 0.1 M I₂ and 10 mM TBP in CH₃CN. Dipping time was 6 h. Active area of 0.22 cm² and measurements were carried out under 1 sun intensity (100 mW/cm²), ^bby dye desorption method, carried out in 2M ethanolic HCl at

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 V_{oc} of **NSQ1-3** suggests that the incorporation of fused donor unit and branched alkyl groups into the dye structure would be a meaningful approach to improve the PCE of metal-free squaraine dyes.

2.6. Electrochemical Impedance Spectroscopy

To understand the effect of fused donor and out-of-plane branched alkyl groups on photovoltaic performance of NSQ dye cells, EIS analysis was carried out in the dark with applied potential. Generally, V_{oc} and J_{sc} of dye cells are known to be affected by the charge recombination dynamics at the interface of TiO₂/dye/electrolyte.⁴⁸ V_{oc} of dye cell is determined by the difference between quasi-Fermi level of TiO_2 ($E_{F,n}$) and Fermi level ($E_{F,redox}$) of the redox couple (I^{-}/I_{3}^{-} in this study), as expressed in Equation 1. The uncertainty of the photo-voltage originates from a shift of the TiO_2 electron quasi-Fermi-level, **Equation 2**, where k_B is the Boltzmann constant, T is the absolute temperature (293 K), n_c the free electron density, and N_c the density of accessible states in the conduction band, which may be ascribed to two major reasons: i) a shift in the TiO₂ conduction band edge (E_{CB}), which can be inferred from the chemical capacitance (C_{μ}), and ii) a fluctuation of electron density, which is related to the electron lifetime (τ) determined by the charge recombination rate.²⁶ Thus, through Nyquist and Bode plots of EIS analysis, corresponding charge transfer resistance (R_ct), ${\it C}_\mu$ and τ is

$$V_{oc} = E_{\rm F,redox} - E_{\rm F,n} \tag{1}$$

$$E_{\rm F,n} = E_{CB} + k_B T \ln\left(\frac{n_c}{N_c}\right) \tag{2}$$

elucidated to explain the charge transfer process at $TiO_2/dye/electrolyte$ interface.

Nyquist plot of NSQR and NSQ1-3 dye cells is shown in Figure 8a, the second semi-circle representing the charge transfer reaction at the TiO₂/dye/electrolyte interface for NSQ3 was larger than other dyes, in the order of NSQ3>NSQ2>NSQ1>NSQR. The peak frequency of Bode plot has shifted towards the lowest value for NSQ3 as shown in Figure 8b. In general, a long electron life time implies slower electron recombination rate at the interface, which increases the free electron density and these observation points the effective passivation of surface by hydrophobic alkyl chains near to TiO₂ surface through van der Waals interaction. Figure $\boldsymbol{8c}$ and $\boldsymbol{8d}$ shows observed \boldsymbol{R}_{ct} and τ respectively, extracted after fitting the Nyquist plot using an equivalent circuit (inset Figure 8c). The τ value of NSQ3 is longer than NSQR, NSQ1 and NSQ2, and which is consistent with observed improvement in $V_{\rm oc}$. Strong π - π interaction and better screening of oxide



Figure 8. Plots of EIS analysis of NSQ dye cells. (a) Nyquist plot (b) Bode plot, (c) and (d) R_{ct} and τ as a function of voltage, respectively.

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Figure 9. OCVD profile of DSSCs based on NSQR and NSQ1-3 sensitizers.

surface showed maximum τ around 52 ms at applied bias of -0.3 V. Under same condition, NSQ1 and NSQ2 showed τ of 13.8 and 29.5 ms, respectively, indicating increase in charge recombination rates. NSQs increased R_{ct} and C_{μ} (Figure S51) further supported the high J_{sc} and V_{oc} values than NSQR. Increase in rate of electron injection and reduced interfacial recombination could bring the difference in electron density in conduction band of metal oxide.⁴⁹ Overall, the successful approach towards increasing the efficiency of unsymmetrical squaraine dyes discussed here could improve further by focusing on V_{oc} . 50 Overall performance of NSQ3 shows an approach to design co-adsorbent free unsymmetrical squaraine dye cells with high efficiency.

2.7. Open-circuit voltage decay measurement

Furthermore, transient recombination kinetics of NSQs were studied after illuminating the device. Open-circuit voltage decay-time profile reflects the electron recombination kinetics after generating triiodide at $TiO_2/dye/electrolyte$ interface.⁵¹ Equation 3 was used to evaluate the correlation between V_{oc}

$$\tau_{\rm n} = -\frac{k_B T}{e} \left(\frac{dV_{oc}}{dt}\right)^{-1} \tag{3}$$

decay and electron lifetime (τ_n) , where k_BT the thermal energy and e is is the positive elementary charge:

According to this equation, the electron lifetime of the devices can be extracted from the slope of the photovoltage decay curves. Voc decay traces were measured in the dark after illuminating the cell for 10 s at 1 sun intensity. Figure 9 shows the decay profile of NSQR and NSQ1-3 dye cells, NSQ3 dye cell shows the slowest decay (78% at 50 s) and NSQR displays the fast voltage decay (95% at 50 s). Remarkably, the minimum

rate of recombination in NSQ3 sensitized dye cell was attributed to the effective passivation of mesoporous surface by introducing hydrophobic alkyl functionalities near to the anchoring group. The observed 120 mV difference in the V_{oc} of NSQ3 compared to NSQR without any co-adsorbent indicates the slow recombination of injected electron with triiodide. Results of FIS experiment in the dark and OCVD measurement in the presence of light in turn supports the deceleration of charge recombination, via dark reaction and back electron transfer, for NSQ3 dye compared to other NSQs.

3. CONCLUSION

The effects of HT and TPA donor moieties and types of alkyl functionalities in unsymmetrical squaraine dyes for dyesensitized solar cell were investigated. Heterotriangulene based NSQ1-3 sensitizers have shown significant improvement in PCE than NSQR, NSQ3 sensitized device achieved an efficiency of 6.73% without co-adsorbent, and in presence of CDCA NSQ2 and NSQ3 exhibited 7.4% and 7.17% PCE, respectively. Higher and broader IPCE of NSQ1-3, due to extended conjugation and strong donor-acceptor coupling, shows the better NIR light harvesting efficiency of these metalfree dyes than NSQR. The EIS and OCVD studies were proved that alkyl-functionalized indolium unit attached to carboxylic acid suppresses the undesirable charge recombination and prolongs the electron lifetime, and hence significantly enhancing the PCE. As a result, NSQ1-3 exhibited an efficiency of more than 70% over reference sensitizer NSQR, PCE of 4.6%. This study suggests that introducing an out-of-plane alkyl chain on indolium group of unsymmetrical squaraine increases the J_{sc} and V_{ac} , and avoiding the co-adsorbent from dye cell fabrication. Hydrophobic alkyl functionalities on squaraine chromophore near to the surface of TiO2 leads to better control over the recombination process between electrolyte and TiO₂.

4. EXPERIMENTAL SECTION

4.1. Materials and Characterization

All reagents were purchased from commercial sources. Solvents were dried and distilled immediately prior to use by standard procedures. All reactions were carried out under an argon atmosphere. Characterizations of all compounds are provided in supporting information. ¹H NMR and ¹³C NMR were recorded in, $CDCl_3$, $MeOH-d_4$ or $DMSO-d_6$ on 200 MHz NMR, 400 MHz NMR and 500 MHz NMR spectrometers. Highresolution mass spectrometric measurements were carried out using the ESI method and an ion-trap mass analyzer. Absorption spectra were recorded at room temperature in Published on 08 November 2016. Downloaded by Freie Universitaet Berlin on 09/11/2016 05:12:23

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Analytik UV-Visible quartz cuvette using Jena Electrochemical measurement was spectrophotometer. carried out using a Bio-Logic potentiostat (model no: SP300). The cyclic voltammetric analysis (CV) was carried out in dry acetonitrile solvent by using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte and Fc/Fc^{+} as internal reference. The experiments were performed at room temperature in nitrogen atmosphere with a three-electrode cell consisting of a platinum foil as counter electrode, an Ag/Ag⁺ reference electrode, and a platinum wire as working electrode.

4.2. Synthetic Procedure

4,4,8,8,12,12-Hexamethyl-4*H*,8*H*,12*H*-benzo[1,9]quinolizino [3,4,5,6,7,-*defg*]acridine (HBQA,4a)^{52,53} was synthesized using a procedure of previous references.

2-Octyldodecanal (1a)⁵⁴

To a solution of 2-octyldodecan-1-ol (4 g, 13.4 mmol) in CH₂Cl₂ (30 mL), pyridinium chlorochromate (7.2 g, 33.5 mmol) was added and stirred at room temperature for 3 h. The crude mixture was filtered through silica gel column chromatography, washed with pet ether, solvent was evaporated and dried under reduced pressure to afford 1a (2.2 g, 55%) as pale yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ : 9.55 (d, J = 3.2 Hz, 1 H), 2.40 - 2.29 (m, 1 H), 1.62 - 1.56 (m, 2 H), 1.47 - 1.43 (m, 2 H), 1.25 (br. s., 28 H), 0.89 - 0.87 (m, 6 H). ¹³C NMR (100 MHz, CDCl₃) δ: 211.9, 182.8, 161.1, 77.3, 77.2, 76.7, 74.6, 72.1, 45.5, 42.8, 37.4, 34.0, 32.2, 31.9, 31.8, 29.7, 29.6, 29.6, 29.5, 29.5, 29.3, 29.3, 29.3, 29.1, 27.4, 25.6, 25.2, 23.9, 22.7, 14.1. MALDI-TOF (*m*/*z*): [M]⁺ calcd for C₂₀H₄₀O: 296.3079; found: 296.2517.

3-Octyltridecan-2-ol (1b)

2-Octyldodecanal (2 g, 6.74 mmol) was dissolved in dry THF (20 mL) at 0 °C, and then MeMgI (3.37 mL, 10.1 mmol) was slowly added. The mixture was stirred at 0 °C for 2 h, then quenched by adding saturated aqueous solution of ammonium chloride, extracted with ethyl acetate and dried over Na₂SO₄. The organic layer was concentrated under reduced pressure to afford 1b (2.03 g, 97%) as pale yellow liquid. This product was used further without purification. ¹H NMR (200 MHz, CDCl₃) δ : 3.81 (q, *J* = 5.8 Hz, 1 H), 1.70 (br. s., 1 H), 1.26 (br. s, 33 H), 1.12 (d, *J* = 6.3 Hz, 3 H), 0.94 - 0.84 (m, 6 H). ¹³C NMR (100 MHz, CDCl₃) δ : 69.7, 44.8, 37.4, 32.2, 31.9, 31.9, 30.2, 30.1, 30.1, 30.1, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 29.3, 29.3, 27.4, 27.4, 25.6, 22.7, 19.8, 14.1.

3-Octyltridecan-2-one (1c)

To a solution of 3-octyltridecan-2-ol (2 g, 6.34 mmol) in CH_2CI_2 (30 mL), pyridinium chlorochromate (2.76 g, 12.68 mmol) and celite (PCC: celite, 1:1, 2.76 g) were added and stirred at room temperature for 4 h. The reaction mixture was filtered through silica gel column chromatography, washed with dichloromethane, solvent was evaporated and purified by column chromatography to afford 1c (1.1 g, 56%) as colorless

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liquid. ¹H NMR (200 MHz, CDCl₃) δ : 2.45 - 2.32 (m, 1 H), 2.06 (s, 3 H), 1.57 - 1.48 (m, 2 H), 1.42 - 1.30 (m, 2 H), 1.21 (br. s, 28 H), 0.88 - 0.78 (m, 6 H). ¹³C NMR (100 MHz, CDCl₃) δ : 212.9, 53.3, 31.8, 31.8, 31.7, 29.7, 29.5, 29.4, 29.4, 29.3, 29.2, 29.1, 28.5, 27.4, 22.6, 14.0. HRMS (ESI): m/z calcd for C₂₁H₄₃O ([M+H]⁺): 311.3314. Found: 311.3308.

2,3,3-Trimethyl-3H-indole-5-carboxylic acid (2a)

4-Hydrazinobenzoic acid hydrochloride (4 g, 21.2 mmol) and 3methyl-2-butanone (3.92 mL, 36.69 mmol) were dissolved into glacial acetic acid (40 mL) and refluxed under nitrogen for 16 h. The mixture was cooled and the solvent was removed under reduced pressure. The residue was dissolved by adding CH₂Cl₂, and then washed with saturated solution of NaHCO₃ and dried over Na₂SO₄. The organic layer was concentrated to afford 2a (3.1 g, 72%) as a light red solid. ¹H NMR (200 MHz, CDCl₃) δ : 10.56 (br. s., 1 H), 8.15 (dd, *J* = 8.1, 1.6 Hz, 1 H), 8.07 (d, *J* = 1.6 Hz, 1 H), 7.69 (d, *J* = 8.1 Hz, 1 H), 2.39 (s, 3 H), 1.37 (s, 6 H). ¹³C NMR (100 MHz, CDCl₃) δ : 192.5, 170.9, 156.9, 145.4, 130.7, 127.2, 123.2, 119.5, 53.8, 22.8, 15.4. HRMS (ESI): m/z calcd for C₁₂H₁₄NO₂ ([M+H]⁺): 204.1025. Found: 204.1019.

3-Decyl-2-methyl-3-octyl-3H-indole-5-carboxylic acid (2b)

4-Hydrazinobenzoic acid hydrochloride (0.6 g, 3.18 mmol) and 3-octyltridecan-2-one (1.18 g, 3.82 mmol) were dissolved into glacial acetic acid (12 mL) and refluxed under nitrogen for 12 h. The mixture was cooled and the solvent was removed under vacuum. The crude product was extracted with CH₂Cl₂, washed with saturated solution of $NaHCO_3$, dried over Na_2SO_4 and solvent was evaporated. The reaction mixture was purified by silica gel chromatography to afford 2b (0.74 g, 54%) as a light red liquid. ¹H NMR (400 MHz, CDCl₃) δ : 11.78 (br. s., 1 H), 8.17 (dd, J = 8.0, 1.6 Hz, 1 H), 7.99 (s, 1 H), 7.70 (d, J = 8.0 Hz, 1 H), 2.33 (s, 3 H), 2.02 - 1.88 (m, 2 H), 1.83 - 1.71 (m, 2 H), 1.25 -1.07 (m, 24 H), 0.85 - 0.80 (m, 6 H), 0.75 - 0.65 (m, 2 H), 0.61 -0.52 (m, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ: 191.4, 171.2, 158.4, 142.2, 130.7, 127.1, 123.3, 119.2, 63.0, 36.9, 31.8, 31.7, 29.7, 29.5, 29.5, 29.4, 29.3, 29.3, 29.2, 29.1, 29.1, 23.5, 22.6, 22.5, 16.0, 14.0, 14.0. HRMS (ESI): m/z calcd for C₂₈H₄₆NO₂ ([M+H]⁺): 428.3529. Found: 428.3523.

5-Carboxy-1,2,3,3-tetramethyl-3H-indol-1-ium iodide (3a)

In a 50 mL round bottom flask, 2,3,3-trimethyl-3H-indole-5carboxylic acid (1.5 g, 7.38 mmol) and 1-iodomethane (1.15 mL, 18.45 mmol) were dissolved in MeCN (12 mL), and refluxed under nitrogen for 16 h. The solvent was evaporated and the crude product was washed with diethyl ether to afford 3a (1.2 g, 75%) as red solid. ¹H NMR (400 MHz, DMSO-*d₆*) δ : 8.37 (s, 1 H), 8.18 (d, *J* = 8.2 Hz, 1 H), 8.02 (d, *J* = 8.2 Hz, 1 H), 3.99 (s, 3 H), 2.81 (s, 3 H), 1.57 (s, 6 H). ¹³C NMR (100 MHz, DMSO-*d₆*) δ : 199.0, 166.5, 145.3, 141.9, 131.6, 130.4, 124.2, 115.4, 54.3, 35.0, 21.5, 14.6. HRMS (ESI): m/z calcd for C₁₃H₁₆NO₂ (M⁺): 218.1176. Found: 218.1176.

5-Carboxy-1-hexyl-2,3,3-trimethyl-3H-indol-1-ium iodide (3b)

In a 50 mL round bottom flask, 2,3,3-trimethyl-3H-indole-5-carboxylic acid (1.5 g, 7.38 mmol) and 1-iodohexane (2.72 mL,

18.45 mmol) were dissolved in MeCN (12 mL) and refluxed under nitrogen for 16 h. The solvent was evaporated and the crude product was washed with diethyl ether to afford 3b (1.7 g, 80%) as red solid. ¹H NMR (200 MHz, DMSO-*d*₆) δ : 8.39 (br. s., 1 H), 8.25 - 8.04 (m, 2 H), 4.54 - 4.35 (m, 2 H), 2.89 (br. s., 3 H), 1.57 (br. s., 6 H), 1.32 (d, *J* = 7.7 Hz, 8 H), 0.93 - 0.83 (m, 3 H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 192.9, 167.4, 155.6, 145.7, 129.7, 127.7, 122.9, 118.7, 53.6, 22.2, 21.9, 15.4, 13.8. HRMS (ESI): m/z calcd for C₁₈H₂₆NO₂ (M⁺): 288.1958. Found: 288.1958.

5-Carboxy-3-decyl-1-hexyl-2-methyl-3-octyl-3H-indol-1-ium iodide (3c)

3-Decyl-2-methyl-3-octyl-3H-indole-5-carboxylic acid (0.7 g, 1.64 mmol) and 1-iodo-hexane (0.48 mL, 3.27 mmol) were dissolved in MeCN (10 mL) in a 25 mL round bottom flask and refluxed at 100 °C under nitrogen for 72 h. The solvent was evaporated and the crude product was purified by silica gel chromatography to afford 3-decyl-1-hexyl-3-methyl-2-methyleneindoline-5-carboxylic acid (0.35 g, 42%) as a light red liquid. ¹H NMR (200 MHz, CDCl₃) δ : 7.96 (dd, *J* = 1.5, 8.3 Hz, 1 H), 7.68 (d, *J* = 1.5 Hz, 1 H), 6.50 (d, *J* = 8.3 Hz, 1 H), 4.12 (s, 1 H), 3.87 (s, 1 H), 3.53 (t, *J* = 7.1 Hz, 2 H), 1.85 - 1.44 (m, 6 H), 1.40 - 1.02 (m, 35 H), 0.86 (dd, *J* = 2.7, 6.0 Hz, 6 H), 0.73 - 0.58 (m, 2 H).

In a 25 mL RB flask, 3-decyl-1-hexyl-3-methyl-2methyleneindoline-5-carboxylic acid (0.25 g, 0.49 mmol) was added in dry diethyl ether (5 mL). Then hydroiodic acid (57wt% in water, 0.20 mL, 0.98 mmol) was added dropwise. The mixture was stirred at room temperature for 2 h. The diethyl ether was removed in vacuum to give 3c (0.22 g, 88%) as brown liquid. ¹H NMR (500 MHz, CDCl₃) δ : 8.36 (d, J = 8.2 Hz, 1 H), 8.20 (s, 1 H), 7.95 (d, J = 8.2 Hz, 1 H), 4.96 - 4.75 (m, 2 H), 3.15 (s, 3 H), 2.30 - 2.18 (m, 2 H), 2.17 - 2.10 (m, 2 H), 1.99 -1.91 (m, 2 H), 1.60 - 1.45 (m, 2 H), 1.42 - 1.26 (m, 6 H), 1.25 -1.15 (m, 11 H), 1.13 (br. s., 13 H), 0.88 - 0.81 (m, 9 H), 0.72 -0.63 (m, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ: 198.8, 168.3, 145.6, 139.1, 132.1, 131.5, 125.0, 115.9, 64.1, 50.9, 37.3, 31.8, 31.6, 31.3, 29.6, 29.4, 29.2, 29.0, 28.9, 28.6, 26.6, 24.2, 22.6, 22.5, 22.4, 17.5, 14.1, 14.0, 13.9. HRMS (ESI): m/z calcd for C₃₄H₅₈NO₂ (M⁺): 512.4462. Found: 512.4462.

3, 4-Dichlorocyclobut-3-ene-1, 2- dione⁵⁵

Squaric acid (1 g, 8.76 mmol) was dissolved in 15 mL of benzene in a 50 mL round bottom flask. Thionyl chloride (1.27 mL, 17.53 mmol) was added dropwise, after half of the addition was over, a drop of dry DMF was added and then continued the dropwise addition of thionyl chloride at room temperature. The mixture was refluxed for 6 h and cooled to room temperature. Excess of solvent was removed and the

residue was dissolved in hexane and kept in refrigerator to isolate pale yellow crystals of the required 3,4-dichlorocyclobut-3-ene-1,2-dione. (Yield: 0.56 g, 42%).

3-chloro-4-(4,4,8,8,12,12-hexamethyl-8,12-dihydro-4Hbenzo[9,1]quinolizino[3,4,5,6,7-defg]acridin-2-yl)cyclobut-3-ene-1,2-dione (4b)

A mixture of 4,4,8,8,12,12-hexamethyl-8,12-dihydro-4Hbenzo[9,1]quinolizino[3,4,5,6,7-defg] acridine (4a) (1 g, 2.74 mmol) and 3,4-dichlorocyclobut-3-ene-1,2-dione (0.45 g, 3 mmol) in benzene (15 mL) was heated at 80 °C for 24 h in a 50 mL round bottom flask. The resultant reaction mixture was cooled and solvents were removed under reduced pressure and purified by column chromatography to give 3-chloro-4-(4,4,8,8,12,12-hexamethyl-8,12-dihydro-4H-benzo[9,1]

quinolizino[3,4,5,6,7-defg]acridin-2-yl)cyclobut-3-ene-1,2-dione (4b) (0.46 g, 35%) as yellow solid. ¹H NMR (200 MHz, CDCl₃) δ : 8.26 (s, 2 H), 7.48 - 7.37 (m, 4 H), 7.24 - 7.17 (m, 2 H), 1.67 (s, 6 H), 1.64 (s, 12 H). ¹³C NMR (100 MHz, CDCl₃) δ : 195.4, 190.3, 186.9, 175.0, 138.5, 131.2, 130.6, 130.2, 130.1, 124.9, 124.8, 124.3, 123.4,121.1, 35.6, 35.4, 34.3, 32.2. HRMS (ESI): m/z calcd for $C_{31}H_{26}CINO_2Na$ ([M+Na]^{*}): 502.1550. Found: 502.1544.

3-(4,4,8,8,12,12-Hexamethyl-8,12-dihydro-4H-benzo [9,1] quinolizino[3,4,5,6,7-defg]acridin-2-yl)-4-hydroxycyclobut-3-ene-1,2-dione (4c)

A mixture of 3-chloro-4-(4,4,8,8,12,12-hexamethyl-8,12dihydro-4H-benzo[9,1]quinolizino [3,4,5,6,7-defg]acridin-2yl)cyclobut-3-ene-1,2-dione (4b) (0.4 g, 0.83 mmol), acetic acid (5 mL), water (5 mL) and 2 N HCl (2 mL) was refluxed for 16 h in a 50 mL round bottom flask, the resultant mixture was concentrated under reduced pressure, and washed with aq. NaHCO₃(50 mL) and brine (50 mL) to give 3-(4,4,8,8,12,12hexamethyl-8,12-dihydro-4H-benzo[9,1] quinolizino [3,4,5,6,7defg]acridin-2-yl)-4-hydroxycyclobut-3-ene-1,2-dione (4c) (0.22 g, 57%) as brown solid. ¹H NMR (400 MHz, CDCl₃) δ : 8.28 (s, 2 H), 7.48 - 7.40 (m, 4 H), 7.27 - 7.20 (m, 2 H), 1.69 (s, 6 H), 1.65 (s, 12 H). 13 C NMR (100 MHz, CDCl₃) δ : 195.4, 190.4, 186.9, 175, 138.5,131.2, 130.6, 130.2, 130.1, 124.9, 124.7, 124.3, 123.4, 121.1, 35.6, 35.4, 34.3, 32.1. HRMS (ESI): m/z calcd for C₃₁H₂₈NO₃ ([M+H]⁺): 462.2069. Found: 462.2064.

General procedure for synthesis of NSQ dyes

A mixture of 3-(4,4,8,8,12,12-hexamethyl-8,12-dihydro-4Hbenzo[9,1]quinolizino[3,4,5,6,7-defg]acridin-2-yl)-4-hydroxy cyclobut-3-ene-1,2-dione (4c) (150 mg, 0.32 mmol) and 2a-2c (0.36 mmol, 1.1 eq.) in benzene (3 mL), 1-butanol (3 mL) and pyridine (1mL) was added in 25 mL round bottom flask and refluxed with a Dean-Stark apparatus for 5 h. The resultant

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mixture was concentrated under reduced pressure, then diluted with dichloromethane, dried over Na₂SO₄, and concentrated under vacuum to give a residue, which was purified with dichloromethane/ methanol to give NSQ1-NSQ3 as green solid.

5-Carboxy-2-[[3-[(4,4,8,8,12,12-hexamethyl-8,12-dihydro-4Hbenzo[9,1]quinolizino[3,4,5,6,7-defg]acridine-2-yl)]-4-oxo-2cyclobuten-2-olate-1-ylidene]methyl]-1,3,3-trimethyl-3H-indolium (NSQ1)

Yield: 19%. ¹H NMR (200 MHz, DMSO- d_6) δ : 8.24 (s, 2 H), 8.15 - 8.05 (m, 1 H), 7.78 (d, *J*=8.46 Hz, 1 H), 7.44 - 7.44 (m, 5 H), 7.27 - 7.12 (m, 2 H), 6.26 (s, 1 H), 3.92 (s, 3 H), 1.81 (s, 6 H), 1.60 (br. s., 18 H). ¹³C NMR (100 MHz, DMSO- d_6) δ : 197.2, 191.7, 183.0, 179.5, 178.8,168.3, 145.5, 142.9, 133.8, 130.3, 130.0, 129.9, 129.8, 126.4, 124.8, 124.3, 124.2, 123.8, 123.7, 123.5, 123.5, 121.9, 119.1, 113.1, 91.7, 50.9, 48.6, 35.2, 35.1, 34.0, 33.5, 32.8, 32.8, 32.4, 25.04. HRMS (ESI): m/z calcd for C₄₄H₄₁N₂O₄ ([M+H]⁺): 661.3066. Found: 661.3061.

5-Carboxy-2-[[3-[(4,4,8,8,12,12-hexamethyl-8,12-dihydro-4Hbenzo[9,1]quinolizino[3,4,5,6,7-defg]acridine-2-yl)]-4-oxo-2cyclobuten-2-olate-1-ylidene]methyl]-3,3-dimethyl-1-hexyl-3Hindolium (NSQ2)

Yield: 29%. ¹H NMR (400 MHz, DMSO- d_6) δ : 8.24 (s, 2 H) 8.13 - 8.05 (m, 1 H), 7.79 (d, *J*=8.31 Hz, 1 H), 7.56 - 7.36 (m, 5 H), 7.22 (t, *J*=8.31 Hz, 2 H), 6.28 (s, 1 H), 4.39 (t, *J*=6.60 Hz, 2 H), 1.81 (s, 6 H), 1.61 (s, 6 H), 1.59 (s, 12 H), 1.40 (br. s., 2 H), 1.35 - 1.18 (m, 6 H), 0.84 (t, *J*=6.60 Hz, 3 H). ¹³C NMR (100 MHz, DMSO- d_6) δ : 192.3, 182.8, 179.3, 178.1, 169.2, 166.8, 144.7, 143.1,133.9, 130.3, 129.9, 129.9, 129.8, 128.9, 126.3, 124.8, 124.3, 123.7, 123.7, 121.9, 113.1, 91.2, 50.9, 44.8, 35.2, 34.0, 32.4, 30.8, 27.2, 25.7, 25.2, 21.9, 13.8. HRMS (ESI): m/z calcd for C₄₉H₅₁N₂O₄ ([M+H]⁺): 731.3849. Found: 731.3843.

5-Carboxy-2-[[3-[(4,4,8,8,12,12-hexamethyl-8,12-dihydro-4Hbenzo[9,1]quinolizino [3,4,5,6,7-defg]acridine-2-yl)]-4-oxo-2cyclobuten-2-olate-1-ylidene]methyl]-3-decyl-1-hexyl-3-octyl-3Hindolium (NSQ3)

Yield: 38%. ¹H NMR (400 MHz, CDCl₃) δ : 8.46 (s, 2 H), 8.24 (d, J = 8.8 Hz, 1 H), 8.12 (s, 1 H), 7.45 - 7.40 (m, 5 H), 7.21 (d, J = 8.8 Hz, 2 H), 6.48 (s, 1 H), 4.28 (br. s., 2 H), 3.14 (br. s., 2 H), 2.18 - 2.12 (m, 2 H), 1.86 (t, J = 7.3 Hz, 2 H), 1.70 (s, 12 H), 1.67 (s, 6 H), 1.47 - 1.44 (m, 2 H), 1.11 (br. s., 14 H), 1.05 (br. s., 10 H), 0.88 (t, J = 6.8 Hz, 6 H), 0.79-0.73 (m, 11.7 Hz, 9 H), 0.46 (br. s., 2 H). ¹³C NMR (100 MHz, CDCl₃) δ : 185.3, 180.1, 175.8, 170.0, 147.4, 136.0, 131.1, 130.9, 130.6, 130.3, 127.3, 126.1, 124.4, 124.3,124.1, 123.6, 110.4, 91.7, 60.3, 45.1, 40.2, 39.9, 35.6, 35.4, 34.0, 32.7, 31.8, 31.7, 31.4, 29.7, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 27.8, 26.7, 24.8, 24.1, 22.5, 22.5, 22.4, 14.0, 13.9 . HRMS (ESI): m/z calcd for C₆₅H₈₃N₂O₄ ([M+H]⁺): 955.6353. Found: 955.6347.

3-Chloro-4-(4-(diphenylamino) phenyl) cyclobut-3-ene-1, 2-dione (5b)

In a 50 mL round bottom flask, a mixture of triphenylamine (5a) (0.8 g, 3.3 mmol) and 3, 4-dichlorocyclobut-3-ene-1, 2dione (0.54 g, 3.6 mmol) in benzene (15 mL) was heated at 80 °C for 24 h. The resultant reaction mixture was evaporated under reduced pressure to give residue, which was purified by column chromatography to give 3-chloro-4-(4-(diphenylamino) phenyl) cyclobut-3-ene-1, 2-dione (5b) (0.45 g, 38%) as yellow solid. ¹H NMR (500 MHz, CDCl₃) δ : 8.07 (m, *J*=9.16 Hz, 2 H), 7.42 - 7.35 (m, 4 H), 7.27 - 7.18 (m, 6 H), 7.02 (m, *J*=9.16 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ : 195.3, 190.4, 186.7, 174.6, 153.8, 145.2, 130.8, 129.9, 126.7, 126.0, 118.6, 118.0. HRMS (ESI): m/z calcd for C₂₂H₁₄CINO₂Na ([M+Na]⁺): 382.0611. Found: 382.0605.

3-(4-(Diphenylamino) phenyl)-4-hydroxycyclobut-3-ene-1, 2-dione (5c)

In a 50 mL round bottom flask, a mixture of 3-chloro-4-(4-(diphenylamino) phenyl) cyclobut-3-ene-1, 2-dione (5b) (0.4 g, 1.1 mmol), acetic acid (7 mL), water (7 mL) and 2 N HCl (2 mL) was refluxed for 16 h, the resultant mixture was concentrated under vacuum to give residue. The residue was washed with NaHCO₃ aq. and brine to give 3-(4-(diphenylamino) phenyl)-4-hydroxycyclobut-3-ene-1, 2-dione (5c) (0.23 g, 61%) as brown solid. ¹H NMR (400 MHz, CDCl₃) δ : 8.07 (d, *J*=8.80 Hz, 2 H), 7.42 - 7.34 (m, 4 H), 7.25 - 7.18 (m, 6 H), 7.02 (d, *J*=8.80 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ : 195.3, 190.4, 186.8, 174.7, 153.8, 145.2, 130.8, 129.9, 126.7, 126.0, 118.6, 118.0. HRMS (ESI): m/z calcd for C₂₂H₁₆NO₃ ([M+H]⁺): 342.1130. Found: 341.1125.

5-carboxy-2-[[3-[N,N-diphenyl-anilin-4-yl]-4-oxo-2-cyclobuten-2olate-1-ylidene] methyl]-3, 3-dimethyl-1-hexyl-3H-indolium (NSQR)

A mixture of 3-(4-(diphenylamino) phenyl)-4-hydroxycyclobut-3-ene- 1, 2-dione (5b) (0.15 g, 0.44 mmol) and 2b (0.14 g, 0.48 mmol, 1.1 eq.) in benzene (5 mL), 1-butanol (5 mL) and pyridine (0.5 mL) was added in 25 mL RB flask and refluxed with a Dean-Stark apparatus for 5 h. The resultant mixture was concentrated under reduced pressure, washed with 2 N HCl, extracted with dichloromethane and dried over Na₂SO₄, then concentrated under vacuum to give a residue, which was purified with dichloromethane/ methanol to give NSQR as blue solid (67 mg, 25%). ¹H NMR (200 MHz, DMSO- d_6) δ : 8.22 (s, 1 H), 8.11 - 7.95 (m, 3 H), 7.78 (d, J=8.84 Hz, 1 H), 7.45 - 7.31 (m, 4 H), 7.24 - 7.08 (m, 6 H), 6.92 (d, J=8.84 Hz, 2 H), 6.24 (s, 1 H), 4.39 (br. s., 2 H), 1.76 (s, 6 H), 1.45 - 1.16 (m, 8 H), 0.87 - 0.79 (m, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ: 192.67, 182.7, 179.0, 178.0, 169.8, 166.8, 149.8, 145.9, 144.7, 143.0, 130.3, 129.9, 128.9, 128.3, 125.8, 125.0, 123.9, 123.6, 120.1, 113.0, 91.2, 50.9, 30.8, 27.2, 25.7, 25.2, 21.9, 13.8. HRMS (ESI): m/z calcd for C₄₀H₃₉N₂O₄ ([M+H]⁺): 611.2910. Found: 611.2904.

4.3. Solar cells preparation and characterization

FTO (F-doped SnO₂ glass; 6 - 8 Ω /sq; Pilkington TEC 7) was cleaned by mucasol (2 % in water), deionised water, and ethanol, successively. To grow a TiO₂ under layer, the substrate was immersed in freshly prepared 50 mM TiCl₄

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aqueous solution at 70 °C for 30 min, and washed with deionised water before drying at 100 °C for 10 min. A paste of TiO₂ nanocrystal (< 20 nm, Ti-Nanoxide T/SP, Solaronix) was deposited by the doctor-blade technique on TiO₂ buffer layer coated FTO substrate, kept in air for 5 min and then annealed at 125 $^{\circ}$ C in air for 15 min. The films were about 6 - 8 μ m thick. The annealed films were coated with scattering layer TiO₂ paste (WER2-O, Dyesol) and annealed at 125 °C in air for 15 min. The annealed films were sintered at 325 °C for 5 min, 375 $^{\circ}\text{C}$ for 5 min, 450 $^{\circ}\text{C}$ for 15 min and 500 $^{\circ}\text{C}$ for 15 min with heating rate of 5 °C per min in air. After reaching the furnace temperature at 50 °C, sintered films were immersed in freshly prepared 50 mM aqueous TiCl₄ solution at 70 $^{\circ}$ C for 30 min. After sintering the TiCl₄-treated TiO₂ films at 500 °C for 30 min, they were immediately immersed in 0.1 mM NSQ dye solution in dichloromethane for 2.5 h, washed and dried at 80 $^{\circ}$ C. In case of CDCA added experiments, different ratio of CDCA added to 0.1 mM dye solution and photoanode dipped for 2.5 h. Sandwich type cell configuration was completed using platinum as cathode, 0.5 M DMII, 0.1 M Lil, 0.1 M I₂ and 10 mM TBP in CH₃CN was used as electrolyte and 25 μ m spacer. *I*-V characteristics of the cells were measured using Keithley digital source meter (2420, Keithley, USA) controlled by a computer and standard AM 1.5 solar simulator (PET, CT200AAA, USA). To measure the photocurrent and voltage, an external bias of AM 1.5 G light was applied using a xenon lamp (450 W, USHIO INC, Philippines) and recorded. IPCE measurements were carried out with a Newport QE measurement kit by focusing a monochromatic beam of light from 300 W Xe lamp onto the devices. The electrochemical impedance spectroscopy (EIS) measurements of the DSSCs were recorded with a Bio-Logic potentiostat (model no: SP300), equipped with an FRA2 module, with different potentials applied in dark. The frequency range explored was 1 mHz to 1 MHz with an ac perturbation of 10 mV. The impedance spectra were analyzed using an equivalent circuit model. OCVD profile was measured with a Bio-Logic potentiostat (model no: SP300), equipped with an FRA2 module, the dye cell was illuminated for 10 sec at 1 sun intensity (100 mW/cm²) and V_{oc} decay recorded in dark.

4.4. Dye desorption from the photoanode

The TiO₂ coated FTO electrodes (0.22 cm², thickness of TiO₂ layer 8+4 μ m) were dipped in 0.1 mM of NSQR, NSQ1-3 in CH₂Cl₂ for 6 h at room temperature, and then washed with CH₂Cl₂ to remove the physisorbed dyes. The electrodes were immersed in 2M ethanolic HCl for 30 min until all the dyes completely desorbed and the amount of adsorbed dye is calculated by UV-Vis experiments.

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