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Simple Metal-Free Organic D-π-A Dyes with Alkoxy- or Fluorine Substitutions: Application in Dye Sensitized Solar Cells

M. Chandrasekharam[1,*], B. Chiranjeevi[1], K. S. V. Gupta[1],
Surya Prakash Singh[1,*], A. Islam[2], L. Han[2], and M. Lakshmi Kantam[1]

[1] Inorganic and Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology, Tarnaka, Hyderabad 500007, India
[2] Photovoltaic Materials Unit, National Institute for Materials Science, 1-2-1, Sengen, Tsukuba, Ibaraki-305-0047, Japan

Two new metal-free organic sensitizers with simplest structural variations have been synthesized for application in nanocrystalline TiO_2 sensitized solar cells. The donor-π-bridge-acceptor (D-π-A) structure dyes, **Y**2 and **Y**3 each designed with three parts, an electron donor unit (substituted phenyl), a linker unit (thiophene), and an anchor unit (cyanoacrylic acid) showed maximal monochromatic incident photon to current conversion efficiencies (IPCE) in a device reaching upto 67% and 82% respectively. The organic sensitizers with 3,4,5-trimethoxy phenyl (**Y**3) as donor moieties obtained better solar light to electrical energy conversion efficiencies of 3.30% where as the organic sensitizer with 2,4-difluoro phenyl as donor (**Y**2) showed comparatively lower efficiency of 1.02%. The efficiency obtained with the reference sensitizer **N**719 under similar fabrication and evaluation conditions was 5.84%.

Keywords: Metal-Free Sensitizers, Nanocrystalline TiO_2, Simple D-π-A Systems, Dye-Sensitized Solar Cells.

1. INTRODUCTION

To replace fast depleting fossil fuels arising from increasing global energy demands the search for clean alternate energy sources is highly demanding.[1–9] The conversion of solar light can be considered as the important renewable energy source that can be tapped for the generation of mass energy. However the unviable production of solar panels from expensive traditional inorganic semiconductors necessitated the search for alternative cheaper solar energy technologies.[10, 11] In this context, since Michael Grätzel introduced high surface area nanoporous TiO_2 films as wide band gap semiconductor, a breakthrough in the area of DSSC, the photovoltaic application of DSSC has been enormously explored because of their low cost and impressive conversion efficiencies.[1a] In DSSC, sensitizers serve as solar light harvesters and their electronic properties influence the light harvesting efficiency and the overall photoelectric conversion efficiency. The ideal sensitizer for DSSC should have high molar extinction coefficient and absorb solar radiation strongly with absorption bands preferably covering a broad range of wavelengths across visible to near IR regions. In addition, the sensitizer should anchor strongly on semiconductor oxide (nanocrystalline TiO_2) surface, to have good electronic communication and inject electrons efficiently into conduction band of TiO_2. Among metal free organic and metal complexes, ruthenium polypyridinie complexes perform better as sensitizers due to their appropriate redox, spectroscopic, and excited-state properties.

There is an intense interest among scientific community to develop metal free sensitizers[5] as alternative to conventional ruthenium complexes in dye sensitized solar cells (DSSCs). The advantages of using metal-free organic sensitizers are (1) The availability of diverse molecular structures that can be easily designed and synthesized. (2) cost effective easy purification and environmentally benign compared to noble metal complexes. (3) high molar extinction coefficients and therefore suitable for good light harvesting efficiency with thinner TiO_2 films. To date, organic dyes exhibit higher efficiencies compared with that of Ru complexes in *p*-type DSCs. Generally, donor-π-bridge-acceptor (D-π-A) structure is the common character of these organic dyes. With these features it is easy to design new dye structures, extend the absorption spectra, adjust the HOMO and LUMO levels and complete the intramolecular charge separation.

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*Authors to whom correspondence should be addressed.

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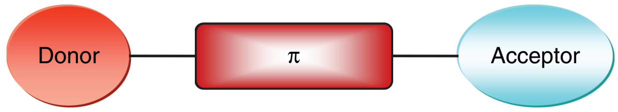


When a dye absorbs light, intramolecular charge transfer occurs from subunit **D** to **A** through the π-bridge. For n-type DSSCs, the excited dye injects the electron into the conduction band of the semiconductor via the electron acceptor group, **A**. However, in p-type DSSCs, the excited dye captures the electron from the valence band of the semiconductor to complete the interfacial charge transfer. Many efforts have been made to change the different parts of organic dyes to optimize DSSC performance such as sensitizers based on polyene-triphenylamine, coumarin, and indoline moieties.

New less volatile redox systems such as ionic liquids[6–9] and hole conductors[10–12] demand thinner TiO_2 films because of mass transport limitations or insufficient pore filling. A great variety of organic sensitizers based on polyene-triphenylamine,[13–19] coumarin,[20–22] and indoline[23–26] moieties give respectable conversion efficiencies of 5–9% with the traditional iodide/triiodide redox system. The introduction of long alkyl chains into donor units can improve the photovoltaic performance and stability of the organic dyes.[27] However, still a better fundamental understanding of the energetic, kinetic and geometric interplay between the oxide/dye/electrolyte constituents is needed in order to design new efficient and stable organic sensitizers for future devices. In continuation of our efforts for the synthesis and photovoltaic evaluation of new sensitizers including ruthenium-complexes, metal-free organic and tetrapyrroles for DSSC applications, we became interested in the synthesis of metal-free organic dyes with fluorine and trimethoxy substituted aryls as donors.[28] We report here design, synthesis and characterization of two new sensitizers and evaluation of the photovoltaic performance of the simplest and smallest possible metal-free organic dyes **Y**2 and **Y**3 for application in nanocrystalline TiO_2 sensitized solar cells and compared with standard **N**719 dye under similar fabrication and measurement conditions (Fig. 1).

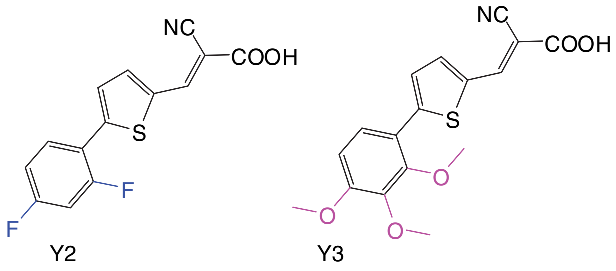


Fig. 1. Structures of the new metal-free organic sensitizers.

2. EXPERIMENTAL SECTION

2.1. Synthesis and Characterization of Sensitizers

All reagents were purchased from sigma-Aldrich. The ^1H NMR and ^{13}C NMR spectra of solutions in $CDCl_3$ and DMSO were recorded on 300 and 500 MHz NMR spectrometers. Chemical shifts were referenced relative to TMS. The IR spectra were recorded on FTIR-5700 spectrometer. Absorption spectra were recorded on a Perkin-Elmer spectrofluorometer.

2.1.1. Synthesis of 5-(2, 4-Di-Fluorophenyl), Thiophene-2-Carbaldehyde (1a)

5-formyl 2-bromo thiophene (0.100 g, 0.523 mmol), 2, 4-difiuoro phenyl boronicacid (0.090 g, 0.575 mmol), 2 M aqNa_2CO_3 (3 ml), Pd [P $(PPh_3)]_4$ (0.060 g, 10 mol%) and dimethoxyethane (3 ml) were mixed and degassed. The whole system was refluxed for 5 h under the inert atmosphere of argon. Then the reaction mixture obtained was filtered through celite, extracted with dichloromethane, dried over Na_2SO_4 and was finally purified by column chromotography on silica gel eluting with ethyl acetate-petroleum ether. Crystalline yellow colored solid was obtained. Yield: 0.090 g (76%).

^1H NMR (300 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.73 (d, $J=$ 3.9 Hz, 1H), 7.69–7.61 (m, 1H), 7.48 (dd, $J=1.3$, 3.9Hz, 1H), 7.02–6.92 (m, 2H), MS (FAB) m/z 428.2.

Synthesis of Y2

To the acetic acid (2 ml) solution of 5-(2, 4-difluorophenyl) thiophene-2-carbaldehyde (0.050 g, 0.223 mmol) cyanoaceticacid (0.018 g, 0.223 mmol), ammonium acetate (5 mol%) were added and was refluxed well for 2 h. The solid obtained was washed thoroughly with water (to remove excess of acetic acid and cyanoaceticacid), hexane and finally with 10% (ethylacetate+hexane) mixture to afford a fine yellow colored solid, **Y**2 (0.060 g, 93%)

^1H NMR (300 MHz, d_6-DMSO) δ 8.30 (s, 1H), 7.83–7.54 (m, 3H), 7.06–7.03 (m, 2H).

2.1.2. Synthesis of 5-(2, 3, 4-Trimethoxyphenyl) Thiophene-2-Carbaldehyde (1b)

5-formyl 2-bromo thiophene (0.100 g, 0.5234 mmol), 2, 3, 4,-trimethoxy phenyl boronicacid (0.132 g, 0.628 mmol), 2 M aqNa_2CO_3 (3 ml), Pd [P $(PPh_3)]_4$ (0.060 g, 10 mol %) and dimethoxyethane (3 ml) were mixed and degassed. The whole system was refluxed for 4 h under an inert atmosphere of argon. Then the reaction mixture obtained was filtered through celite, extracted with dichloromethane, dried over Na_2SO_4 and was finally purified by column chromotography on silica gel eluting with ethyl acetate-petroleum ether. Fine yellow colored solid was obtained. Yield: 0.110 g (75%).

^{1}H NMR ($CDCl_3$) δ 9.87 (s, 1H), 7.66 (d, $J = 3.7$ Hz, 1H), 7.43 (d, $J = 3.7$ Hz, 1H), 6.70 (d, $J = 8.30$ Hz, 1H), 3.94 (s, 3H), 3.90 (s, 3H), 3.88 (s, 3H). MS (FAB) *m*/*z* 428.2.

Synthesis of Y3

To the acetic acid (2 ml) solution of 5-(2,3,4-trimethoxyphenyl) thiophene-2-carbaldehyde (0.100 g, 0.3597 mmol), cyanoaceticacid (0.033 g, 0.3597 mmol), and ammonium acetate (5 mol %) were added and was refluxed well for 5–6 h. The solid obtained was washed thoroughly with water (to remove excess of acetic acid and cyanoaceticacid), hexane and finally with 10% (ethylacetate+hexane) mixture (to remove any nonpolar and slightly polar impurities) to afford a fine red colored solid, **Y**3 (0.300 g, 83%)

^{1}**H** NMR (300 MHz, d_6-DMSO) δ 8.24 (s, 1 H), 7.82–7.75 (m, 1 H), 7.54–7.42 (m, 2 H), 6.80 (d, $J = 9.06$, 1 H). MS (FAB) *m*/*z*428.2.

2.2. Preparation of TiO_2 Electrode

Nanocrystalline TiO_2 photoelectrodes of about 20 μm thickness (area: 0.25 cm^2) were prepared using a variation of a method reported by Grätzel and co-workers.[2] Fluorine-doped tin oxide-coated glass electrodes (Nippon Sheet Glass Co., Japan) with a sheet resistance of 8–10 ohm^{-2} and an optical transmission of >80% in the visible range were used. Anatase TiO_2 colloids (particle size ~ 13 nm) were obtained from commercial sources (Ti-Nanoxide D/SP, Solaronix). The nanocrystalline TiO_2 thin films of approximately 20 μm thickness were deposited onto the conducting glass by screen-printing. The film was then sintered at 500 °C for 1 h. The film thickness was measured with a Surfcom 1400A surface profiler (Tokyo Seimitsu Co. Ltd.). The electrodes were impregnated with a 50 mM titanium tetrachloride solution to block the TCO glass electrode to come into direct contact with the electrolyte thus preventing the recombination, and sintered at 500 °C. The dye solutions (2×10^{-4} M) were prepared in 1:1 acetonitrile and *tert*-butyl alcohol solvents. Deoxycholic acid as a co-adsorbent was added to the dye solution at a concentration of 20 mM. The electrodes were immersed in the dye solutions and then kept at 25 °C for 20 h to adsorb the dye onto the TiO_2 surface.

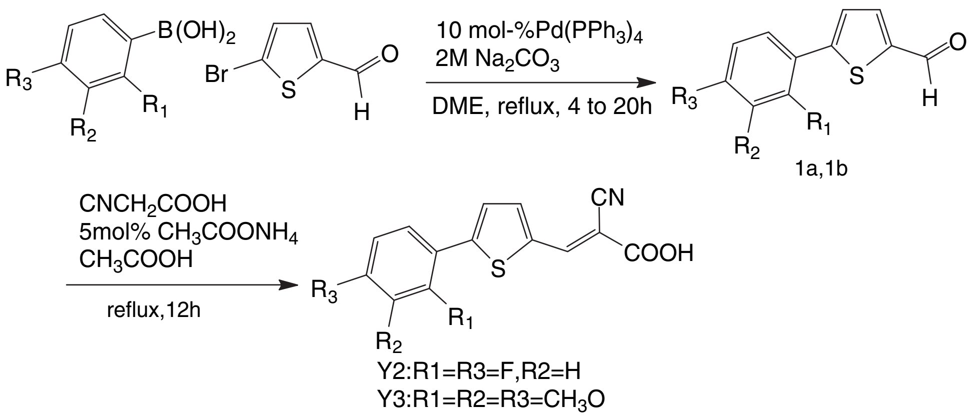
2.3. Fabrication of Dye-Sensitized Solar Cell

Photovoltaic measurements were performed in a two-electrode sandwich cell configuration. The dye-deposited TiO_2 film was used as the working electrode and a platinum-coated conducting glass as the counter electrode. The two electrodes were separated by a surlyn spacer (40 μm thick) and sealed up by heating the polymer frame. The electrolyte was composed of 0.6 M dimethylpropylimidazolium iodide (DMPII), 0.05 M I_2, and 0.1 M LiI in acetonitrile (ACN).

2.4. Photovoltaic Characterization

The working electrode was illuminated through a conducting glass. The current–voltage characteristics were measured using the previously reported method[29] with a solar simulator (AM-1.5, 100 mW/cm^2, WXS-155S-10: Wacom Denso Co., Japan). Monochromatic incident photon-to-current conversion efficiency (IPCE) for the solar cell, plotted as a function of excitation wavelength, was recorded on a CEP-2000 system (Bunkoh-Keiki Co. Ltd.). Incident photon-to-current conversion efficiency (IPCE) at each incident wavelength was calculated from Eq. (1), where I_{sc} is the photocurrent density at short circuit in mA cm^{-2} under monochromatic irradiation, q is the elementary charge, λ is the wavelength of incident radiation in nm, and P_0 is the incident radiative flux in W m^{-2}.

$$\text{IPCE}(\lambda) = 1240\,(I_{sc}/q\lambda P_0) \tag{1}$$



Scheme 1. Synthesis of Sensitizers Y2 and Y3.

3. RESULTS AND DISCUSSION

3.1. Synthesis

Difluorophenyl and trimethoxyphenyl were chosen as donor moieties for the two metal-free organic sensitizers **Y**2 and **Y**3 respectively. Though there are a few reports on the role of fluorine on ruthenium as well as metal-free organic sensitizers, we assumed to synthesize the simplest fluorine substituted sensitizer for DSSC application.[30] In contrast to the reported organic sensitizers where the fluorine has been substituted on the spacer aryl moiety[30d], we chose to substitute fluorine on the donor moiety in **Y**2. On the other hand trimethoxyphenyl is a good electron donating unit selected for **Y**3. The thiophene unit is a conjugation moiety with two double bonds and also provides stability to the molecule by virtue of aromaticity where as cyanoacrylic acid group provides a strong anchor for the sensitizer to electronically bind onto TiO_2 semiconductor particles.

The synthesis of two new organic sensitizers was carried out according to the Scheme 1. 2-bromo-5-formyl thiophene was subjected to Pd catalyzed Suzuki coupling with the corresponding substituted phenyl boronic acid in presence of aq. Na_2CO_3 and dimethoxy ethane. The crude reaction mixture after work up was column chromatographed to obtain pure 2-aryl-5-formyl thiophenes 1a and 1b in good yield. Knoevenagel condensation of the aryl substituted formyl thiophenes with cyanoacetic acid in presence of acetic acid and ammonium acetate for 7 hours under refluxing conditions yielded the crude dye which was purified by recrystallization to give the sensitizers **Y**2 and **Y**3. The formyl thiophenes (1a & 1b) and the sensitizers were characterized by FTIR, ^{1}HNMR and ESI-MASS spectroscopes.

3.2. Electronic Absorption, Emission and Electrochemical Properties

Equimolar dye solutions of **Y**2 and **Y**3 were prepared in dimethylformamide to obtain the molar absorptivities, and the electronic absorption spectra recorded as a function of wavelength were compared with that of **N**719 (Fig. 2). The electronic absorption spectra of **Y**2 and **Y**3 dyes show well defined absorption bands and their molar extinction coefficients (ε) are 31000 $M^{-1}cm^{-1}$ at 355 nm and 42000 $M^{-1}cm^{-1}$ at 378 nm respectively under similar conditions. The molar extinction coefficient (ε) of alkoxy substituted sensitizer (**Y**3) is higher while di-fluoro substituted sensitizer (**Y**2) showed relatively lower value, however much higher molar extinction coefficient than the standard N719, ruthenium complex.

The emission spectra of the new sensitizers were recorded in DMF medium by exciting the complexes with their corresponding absorbance maximum obtained in DMF (Fig. 3). Their emission spectra were analyzed by Gaussian reconvolution method, which enabled to integrate emission peak to estimate their emission maxima centred at 451 and 418 nm for **Y**2 and **Y**3 sensitizers respectively.

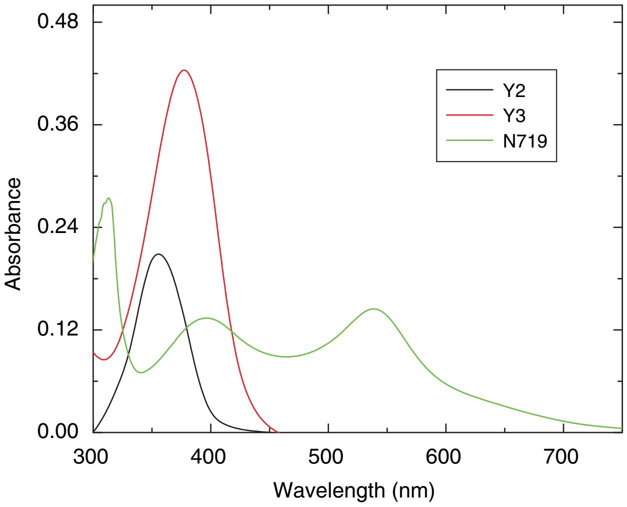


Fig. 2. UV-Visible spectra of Y2, Y3 and N719.

Electrochemical properties of **Y**2 and **Y**3 dyes were scrutinized by cyclic voltammetry using tetra-butyl ammonium perchlorate (0.1 M in acetonitrile) as electrolyte and ferrocene as an internal standard at 0.42 V versus SCE. The reduction potentials obtained for these sensitizers −1.58 V and −1.71 V versus SCE, respectively are more negative (or higher in energy) than the conduction band edge of TiO_2 (−0.80 V versus SCE) providing a thermodynamic driving force to inject electron from the dye to TiO_2.

3.3. Photovoltaic Measurements

The incident photon-to-current conversion efficiencies (IPCEs) of DSSCs constructed based on **Y**2 and **Y**3 sensitizers are plotted as function of excitation wavelength

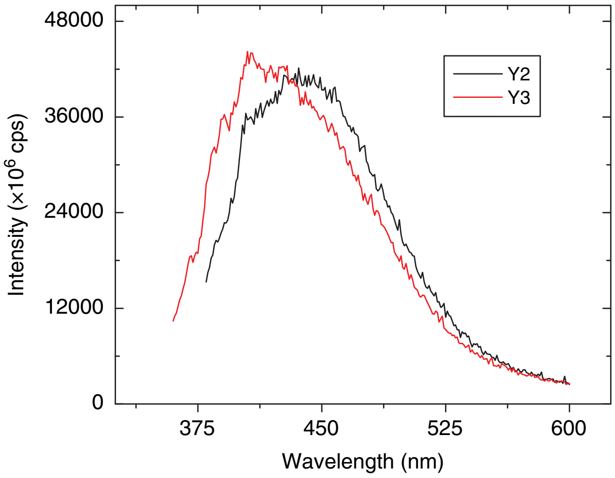


Fig. 3. Emission spectra of Y2 and Y3 sensitizers.

and their IPCE spectra were compared with that of **N**719 sensitized cell. Figure 4 presents the typical photocurrent action spectra of the DSSCs fabricated using the dye solutions (2×10^{-4} M) prepared in 1:1 acetonitrile and *tert*-butyl alcohol solvents. The maximum IPCE observed for these two dyes are within the spectral range of 300–600 nm. The DSSCs constructed based on **Y**2 and **Y**3 sensitizers in combination with the electrolyte composed of 0.6 M dimethylpropyl-imidazolium iodide (DMPII), 0.05 M I_2, and 0.1 M LiI in acetonitrile exceeds IPCE values of 67% and 82% respectively reaching maximum at 425 nm. Considering the light absorption and scattering loss by the conducting glass, the maximum efficiencies for absorbed photon-to-collected electron conversion efficiencies (APCEs) of **Y**2 and **Y**3 sensitizers are almost close to unity over a broad spectral range of 300 to 600 nm.

An electrolyte system containing MPII (0.6 M), I_2 (0.1 M) LiI (0.5 M) and TBP (0.5 M) in methoxypropionitrile was employed to study the photovoltaic performance of the new organic sensitizers in the DSSC test cells with 0.25 cm^2 active area. The IV characteristics of the sensitizers **Y**2 and **Y**3 are shown in Figure 5. Among the two new sensitizers, **Y**3 sensitizer exhibited the best photovoltaic performance $\boldsymbol{J}_{\mathrm{sc}}$ of 6.055 mA/cm^2, $\boldsymbol{V}_{\mathrm{oc}}$ of 716 mV and fill factor of 0.762, yielding an overall power conversion efficiency of 3.30%, at AM 1.5 sunlight, **Y**2 sensitizer exhibited $\boldsymbol{J}_{\mathrm{sc}}$ of 3.214 mA/cm^2, $\boldsymbol{V}_{\mathrm{oc}}$ of 448 mV and fill factor of 0.711, yielding an overall power conversion efficiency of 1.02% (Table I). Under similar conditions, **N**719 sensitized solar cell fabricated using the same electrolyte gave a short-circuit photocurrent density of 17.53 mA/cm^2, an open-circuit photovoltage of 517 mV and fill factor of 0.645, yielding an overall conversion efficiency of 5.84%. To evaluate the effect of electron with drawing difluoro substituted phenyl in the metal free organic sensitizer, we introduced two fluorine atoms in the sensitizer Y2. However, from the photovoltaic parameters obtained it seems that without any electron donating moieties, fluorine alone results in poor performance. Although the **Y**2 and **Y**3 sensitizers show lower IPCE values than that of N719, this problem could be solved using tandem DSSCs, a subject for further study. We are currently investigating the optimization of this series of sensitizers by introduction of various electron-donating groups (alkoxy, TPA, etc.) in the electron donor unit which can extend the absorption towards red region.

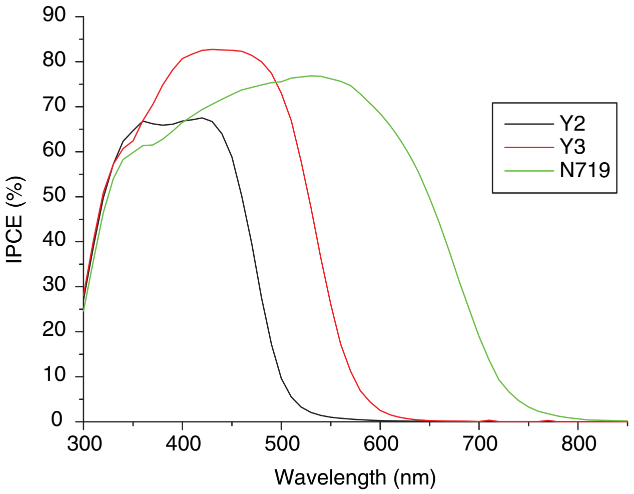


Fig. 4. Photocurrent action spectra (IPCE) of nanocrystalline TiO_2 film (20 μm) sensitized by Y2, Y3 and N719. The redox electrolyte solution was a mixture of 0.6 M DMPII, 0.05 M I2, 0.1 M LiI and 0.3 M TBP in acetonitrile.

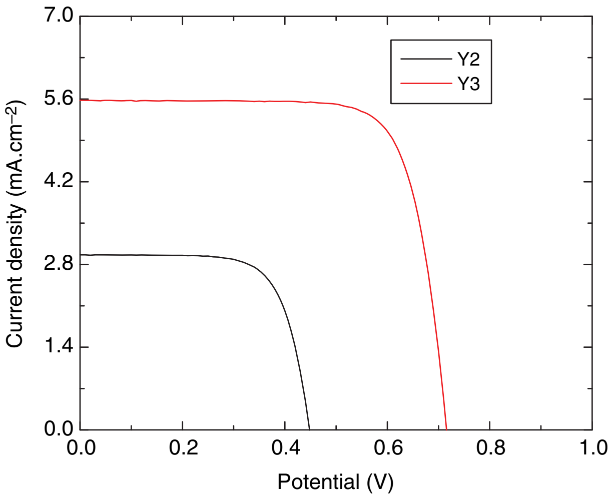


Fig. 5. Photocurrent density versus voltage curves for DSSCs based on Y2 and Y3 under irradiation of AM 1.5 G simulated solar light (100 mW cm^{-2}).

In conclusion, we strategically designed and synthesized two simplest new metal-free organic sensitizers for application in nanocrystalline TiO_2 sensitized solar cells. The monochromatic incident photon to current conversion efficiencies (IPCE) of the sensitizers **Y**2 and **Y**3 in a device reaching upto 67% and 82% were achieved. The organic sensitizer with 3,4,5-trimethoxy phenyl (**Y**3) as donor moiety obtained better solar light to electrical energy conversion efficiencies of 3.30% where as the sensitizer **Y**2 showed comparatively lower efficiency of 1.02%. In contrast to reported sensitizers, these sensitizers are the simplest and particularly **Y**2 has fluorine substituted on donor moiety. The low efficiency of **Y**2 is attributed to the lack of absorption in the region >400 nm. Efforts are on for studying this class of fluoro substituted metal-free organic dyes towards achieving higher solar to electricity conversion efficiency.

Table I. Photovoltaic Performance of DSSCs for Y2 and Y3 dyes compared with N719.

Dye	J_{sc} [mA]	V_{oc} [V]	*ff*	Eff [%]
Y2	3.214	0.448	0.711	1.02
Y3	6.055	0.716	0.762	3.30
N719	17.53	0.517	0.645	5.84

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