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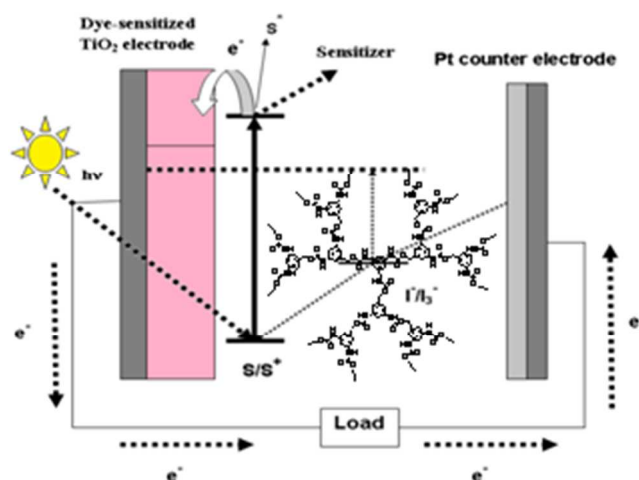
Graphical abstract

Enhanced Performance of Nanocrystalline Dye-Sensitized Solar Cell based on Polyurethane Dendrimers

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Photovoltaic parameters of dye sensitized solar cell (DSSC) fabricated with and without fourth generation polyurethane dendrimers has been discussed.

Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Enhanced Performance of Nanocrystalline Dye-Sensitized Solar Cell based on Polyurethane Dendrimers

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DOI: 10.1039/b000000x

Abstract

The use of novel *p*-chlorophenyl and styrenyl-TEMPO terminated fourth generation (G4) polyurethane dendrimers doped with KI and I₂ in conjunction with N3 dye as an efficient polymer electrolyte to improve the efficiency of nanocrystalline TiO₂ dye-sensitized solar cell (DSSC) has been described. Coordinative interactions and structural changes of these dendritic polymer electrolytes have been characterized by X-ray diffraction (XRD), electrical conductivity and scanning electron microscopic (SEM) studies. The XRD and SEM results confirm the amorphous structure of the electrolytes. The ionic conductivity of doped polyurethane dendrimers was remarkably high and the values were in the range of $1.5 \times 10^{-3} \text{ Scm}^{-1}$ - $1.1 \times 10^{-3} \text{ Scm}^{-1}$ at room temperature. As a consequence, the performance of devices fabricated with dendrimers were appreciably good compared to that fabricated without dendrimers and in one case the photocurrent, photovoltage, fill factor and energy conversion efficiency achieved was 10.6 mA/cm², 900 (mV), 0.51 and 8.5% respectively under simulated sunlight with AM 1.5 at 50 mW/cm².

Introduction

The interest of researchers is ever increasing in order to develop new alternative energy sources with concern about health and environmental issues such as decreasing air pollution and carbon dioxide emission. Considering those facts, solar energy is the vital energy source because it is abundant in nature, it is clean and safe, and it allows energy production in inaccessible areas¹. Regan and Gratzel described interesting properties like transparency and multicolor options, easy integration into building architecture, short energy payback time with potentially low production costs of dye-sensitized solar cells (DSSCs)². Presently, the highest photovoltaic energy conversion efficiency of 12% has been achieved using titanium dioxide nanoparticles as a photo-anode, porphyrin molecules as a sensitizer and cobalt (II/III) as a redox couple³. A DSSC is generally composed of a nano crystalline semiconductor film electrode modified with a dye, a platinum (Pt) counter electrode and an electrolyte solution between the electrodes (anode and cathode). The electrolyte frequently used in DSSC is I⁻/I₃⁻ redox couple in an organic solvent. The DSSC based on liquid electrolyte suffer with several disadvantages like leakage, toxicity and evaporation of electrolyte⁴. Therefore, many efforts have been taken by researchers in order to overcome this problem by replacing liquid electrolytes with organic and inorganic p-type semiconductors as a solid-state charge transport materials, but the efficiency of these cells were inadequate due to low charge transportation and reduced contact with the TiO₂ electrode⁵. Among the different polymer electrolytes used for the DSSCs, the cell fabricated with electron rich nitrogen containing polymer exhibited improved efficiency⁶.

Dendrimers are well-defined and symmetrically branched discrete macromolecules that find interest because of their globular structure at nano scale and their unique properties. Compared to linear polymers, dendrimers exhibit high solubility and low viscosity^{7,8}. The globular shape of dendrimers provides a large surface area that can be decorated with variety of chromophores, resulting in a large absorption cross-section and enabling effective capture of photons⁹. Rajakumar and co-workers synthesized first generation triazole based phenothiazine dendrimer and used for solar energy harvesting application¹⁰. Rumbles and co-workers used CdSe nanoparticle:thiophene dendrimer composite for photovoltaic applications¹¹.

Though polyurethanes are an important class of materials, their dendritic molecules have been studied very poorly due to cumbersome synthetic procedure¹². Recently, we reported hyperbranched polyurethane and hyperbranched polyurea for solar cell applications^{6,13,14}. However, perfect polyurethane dendrimer is not at all reported as solar energy material.

In this paper, we report the performance of nano crystalline TiO₂ DSSC based on higher generation dendrimers for the first time. Fourth generation polyurethane dendrimers with two different end groups are used as electrolyte in combination with KI and I₂. These molecules are basically good electron donors because they have large number of nitrogen atoms in the dendritic skeleton. They can coordinate with the dissociated electrolyte ions thus, the short circuit current density (*J*_{sc}) will be increased.

The large free volume present in-between the numerous branch points of the dendrimer will facilitate the charge transport, consecutively the open circuit photovoltage (V_{oc}) and efficiency of solar cell will be enhanced¹⁵.

5 Experimental

Materials

G4 polyurethane dendrimers were prepared according to the procedures described in our very recent reports^{16,17}. Commercially available acetic acid, [cis-di(thiocyanato)-N,N-bis (2,2'-bipyridyl-4,4'-dicarboxylic acid) ruthenium (II)] dihydrate (N3 dye), tetra isopropyl titanate, triton X-100 and isopropyl alcohol were purchased from Aldrich. Fluorine doped tin oxide (FTO) conducting glasses of sheet resistance 10 Ω /sq.cm were obtained from BHEL, India. Titanium-di-oxide (TiO_2) nanoparticles (P25, \approx 25nm, Degussa AG, Germany), anhydrous iodine (I_2), ethanol (C_2H_5-OH) (99.5%), potassium iodide (KI), N,N-dimethyl formamide (DMF) and acetone were purchased from Merck. All these chemicals were used as received.

Preparation of polyurethane dendrimer electrolytes

In a typical preparation, 0.05 g of G4 polyurethane dendrimer was dissolved in 10 ml of DMF and stirred at room temperature for 1 hr. Then, 0.03g of KI and 0.006g of I_2 were added and the stirring was continued for another 1 hr. The resultant electrolyte solution was used for the fabrication of DSSC.

25 Preparation of TiO_2 electrode and fabrication of dye-sensitized solar cell (DSSC).

Nanocrystalline TiO_2 DSSCs were designed and fabricated according to the procedure described in our previous report¹⁴. First, a semi-colloidal suspension comprising a mixture of glacial acetic acid (5.5 mL), tetra isopropyl titanate $Ti[(CH_3)_2COH]_4$ (5 mL), one drop of triton X-100, iso-propanol (10 mL), water (2 mL) [added drop wise while stirring the solution] and TiO_2 powder (0.7 g) was prepared and was kept under vigorous stirring for 3 – 4 h. Then, nanoporous TiO_2 semiconductor thin films having \sim 9 μ m thickness on FTO conducting glass were prepared by coating a small amount of the suspension on the FTO conducting glass plate by means of a dropper and kept in a hot plate maintained at 423 K and was allowed to dry. The TiO_2 coated conducting glass plate was then sintered at 723 K for 30 min. After sintering, the TiO_2 electrodes were immersed in a solution of an organometallic dye [Cis-di(thiocyanato)-N,N-bis (2,2'-bipyridyl-4,4'-dicarboxylic acid) ruthenium (II)] dihydrate (N3 dye) (5×10^{-5} M) in absolute ethanol for 24 h at 298 K and washed again with absolute ethanol and dried in a moisture-free atmosphere. Finally, blended dendrimer electrolyte solutions (150 μ l) were directly cast onto dye-adsorbed TiO_2 electrodes (photoanode) and evaporated to remove the solvent. Then, the platinum coated FTO glass (coated by sputtering technique) (photocathode) was placed on the face of the photoanode by sandwich method.

Measurements

X-ray diffraction studies

The XRD analyses were performed on thin film specimens of

undoped and doped polymer electrolyte samples using a Bruker D8 Advance X-ray Diffractometer with the radiation source of $CuK\alpha$ ($\lambda=1.541\text{\AA}$) operated at the voltage of 40 kV and current 30 mA. The scanning angle range was 10-80° (2 θ) and the scanning rate was 0.02°/min.

Electrical conductivity studies

The complex impedance data were collected and analyzed systematically using a computer-interfaced Hewlett-Packard Model HP4284A Precision LCR Meter at room temperature (298 K) in the frequency domain 20 Hz – 1 MHz at an applied potential difference of 500 mV. The frequency response of the film corresponds to an equivalent circuit consisting of parallel combination of appropriate circuit elements namely R and C where R and C denote the resistance and capacitance respectively and the resultant intercept of semicircular impedance plot (i.e. plot of Z'' versus Z' where Z' and Z'' represent the real and imaginary parts of the complex impedance Z^*) on the real axis were analyzed by means of Boukamp equivalent circuit program software available internally during each measurement as depicted elsewhere^{18,19}. During such measurements, thin film specimens were sandwiched between two silver discs and the electrical conductivity (σ) of various dendrimer electrolyte samples were determined accurately using the relationship

$$\sigma = \frac{t}{A \cdot R_b} \quad (1)$$

where t is the thickness of the electrolyte film, R_b is the bulk resistance and A is the cross-sectional area of the film membrane²⁰.

Scanning electron microscopic studies

The surface morphology of the un-doped and doped polymer electrolyte samples were observed using a SEM, Hitachi-S 4800N Model with an accelerating voltage of 5,000 V and emission current of 119000 nA. The cross section was obtained by fracturing the sample in liquid nitrogen. It was then vacuum-dried, sputter coated with gold particles upto 30 seconds to minimize charging and attached to a sample holder with the aid of conductive copper tapes.

Photocurrent-photovoltage measurements

The photocurrent-photovoltage diagrams were monitored and recorded using a BAS 100A Electrochemical analyzer unit under illumination area of 1 cm² with tungsten halogen lamp (OSRAM, Germany) of light intensity 50 mW/cm² [EXTECH-33, Light meter with memory] by wrapping remaining area using Teflon coating.

Results and Discussion

100 Polymer matrix

In this study, fourth generation dendritic polyurethanes terminated with *p*-chlorophenyl and styrenyl-TEMPO (TEMPO – 2,2,6,6-tetramethylpiperdinyloxy) groups are used as polymer matrix for DSSC. The structure of the dendrimers is given in Fig. 1. The *p*-chlorophenyl moiety was derived as terminal group at the end of each generation growth by virtue of the synthetic method adopted for the construction of dendrimers. This end

group was replaced with styrenyl-TEMPO moiety with an intention to improve the electrolytic performance of the dendrimer i.e., compared to the nitrogen atom of urethane group, the N-oxy group present in the TEMPO moiety will involve more effectively in the coordinative interaction with the metal salt added, thus the performance of the DSSC will be improved.

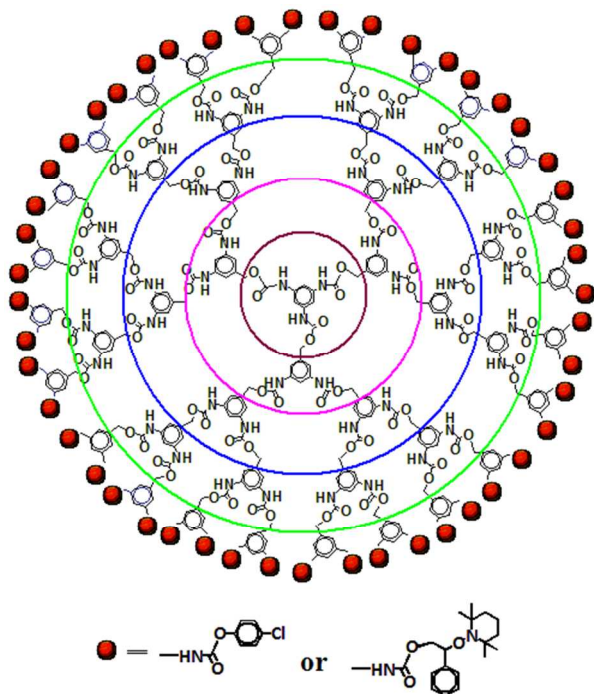


Fig. 1. Structure of *p*-chlorophenyl- and styrenyl-TEMPO-terminated G4 polyurethane dendrimer.

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X-ray diffraction analyses of dendrimer electrolytes.

The X-ray diffraction patterns acquired for pure and doped G4 polyurethane dendrimer terminated with *p*-chlorophenyl group is shown in Fig. 2. It is clear from the figure that pure polyurethane dendrimer shows crystalline peaks in the range of $2\theta = 14.3^\circ - 59.2^\circ$ and they were disappeared and new peaks appeared at $2\theta = 62.6^\circ, 63.2^\circ, 65.4^\circ, 68.5^\circ, 70.5^\circ$ and 72.4° after doping with KI and I_2 ; the new peaks may correspond to $(I_2)^{21}$. This observation indicates that after the addition of dopant KI and I_2 , crystallinity of *p*-chlorophenyl-terminated G4 dendrimer has been decreased considerably, implying the enhancement of amorphous region and consenting the movement of free ions to flow from one site to another site and hence the overall ionic conductivity of the dendrimer electrolyte will be increased and thereby decreasing the I^-/I_3^- diffusion resistance. Moreover, the crystal development in the dendrimer electrolyte is prevented by the coordinative interaction likely occurring between K^+ and nitrogen atom of the dendrimer. Thus, this doped dendrimers would serve as excellent electrolytes for DSSC.

The X-ray diffraction patterns acquired for pure and doped G4 polyurethane dendrimer terminated with styrenyl-TEMPO is shown in Fig. 3. In analogous to the preceding findings, the pure

dendrimer exhibits sharp crystalline diffraction peaks in the range of $2\theta = 23.8^\circ - 48.5^\circ$. All these peaks were disappeared after incorporation of KI and I_2 into dendrimer and several new peaks in the 2θ range of $51.7^\circ - 79.2^\circ$ equivalent to other crystalline phases have been observed in the doped polymer electrolyte. This sort of disappearance of crystalline phases and appearance of new crystalline phases indicates the complete dissolution of dendrimer in I^-/I_3^- redox couple and considerable decrease in the crystallinity of the dendrimer.

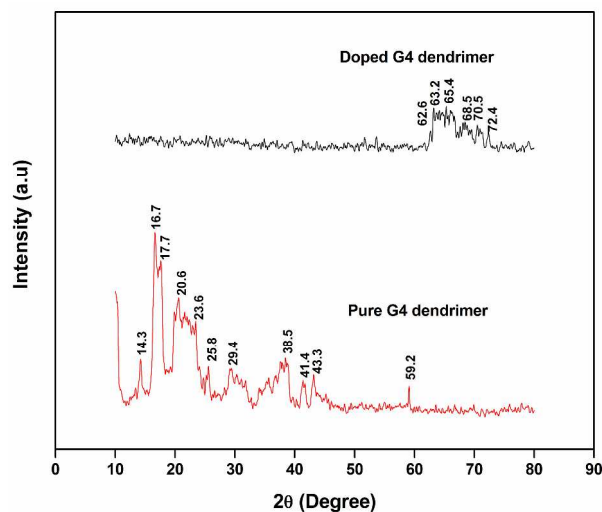


Fig. 2. X-ray diffraction pattern of pure and doped *p*-chlorophenyl-terminated G4 polyurethane dendrimer.

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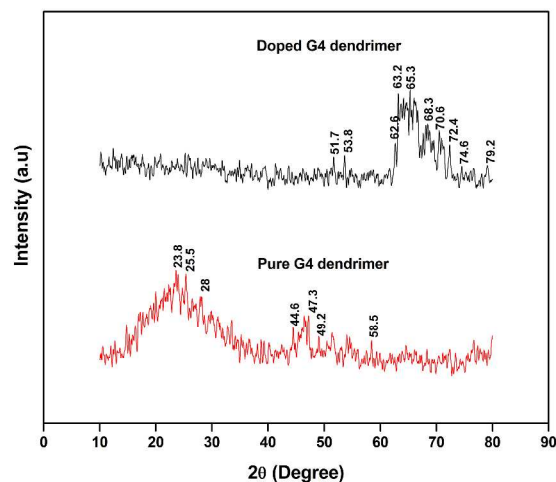


Fig. 3. X-ray diffraction pattern of pure and doped styrenyl-TEMPO-terminated G4 polyurethane dendrimer.

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Morphological analyses of dendrimer electrolytes.

Scanning electron micrographs of pure and doped dendrimers are shown in Fig. 4. The SEM images obtained for un-doped polymer

electrolytes show a collection of distinct spherical particles closely connected to each other. This observation is consistent with the globular shape of the dendrimer molecules. Besides, the smoothened surface with clusters was also seen in the un-doped polymer electrolyte. In the case of doped polymer electrolytes, the micrographs show a porous structure with the disappearance of clusters that are observed for pure dendrimer. This kind of porous structure will allow better penetration of I^-/I_3^- redox couple into dendrimer electrolyte thereby allow movement of ions faster which in turn will increase the ionic conductivity and the performance of nanocrystalline TiO_2 DSSC. In addition, the micro-pores seen in the doped polymer electrolytes are well interconnected with strong pore walls and there is no aggregation in the surface, indicating that the dopant KI and I_2 are homogeneously dispersed in the polymer matrix. It is also noted from the images of doped dendrimer electrolyte that the amorphous region of the polymer matrix was enhanced and it has large number of unevenly sized pores that are responsible for ionic hopping conduction mechanism and hence the electrolyte will show enhanced ionic conductivity.

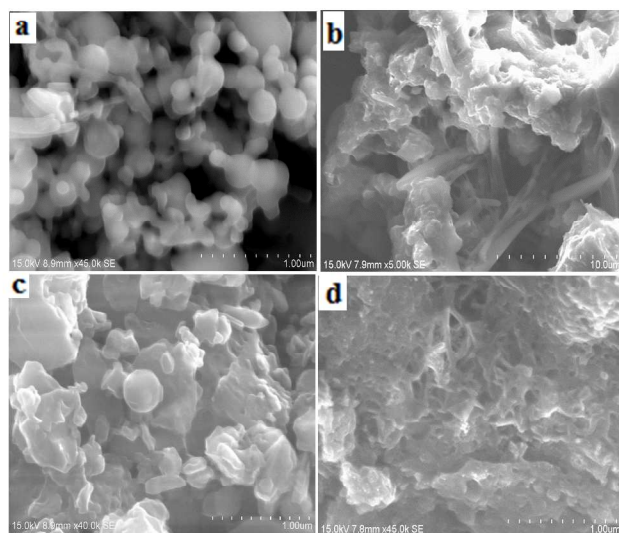


Fig.4. SEM images of (a) pure and (b) doped *p*-chlorophenyl-terminated G4 polyurethane dendrimer; (c) pure and (d) doped styrenyl-TEMPO terminated G4 polyurethane dendrimer.

Electrical conductivity studies

Ambient temperature (298 K) electrical conductivity plots acquired for pure and doped G4 polyurethane dendrimers are shown in Fig. 5 and Fig. 6 respectively. The ionic conductivity values obtained are remarkably high and are given in Table 1. Compared to un-doped dendrimers, doped *p*-chlorophenyl and styrenyl-TEMPO terminated dendrimer electrolytes showed fifteen and thirty three fold high ionic conductivity respectively and this result is consistent with the XRD and SEM observations. This result indicates that the dissociation of the dopant salt occurred effectively and the cations are coordinated with the electron donor atoms (i.e. nitrogen atoms) present in the dendrimer through Lewis acid–base type of interaction. The increase in ionic conductivity is due to solvation–desolvation

process occurring along the chains that take place predominantly in the amorphous phase of the host polymer²². The high ionic conductivity can also be explained with the presence of large free volume within the dendritic skeleton of the molecules that favor the ions to move faster in the dendritic skeleton and makes free space in the conducting pathways. The sustained mobility of charge carriers and enhanced ionic conductivity are important factors required for the high photovoltaic energy conversion efficiency.

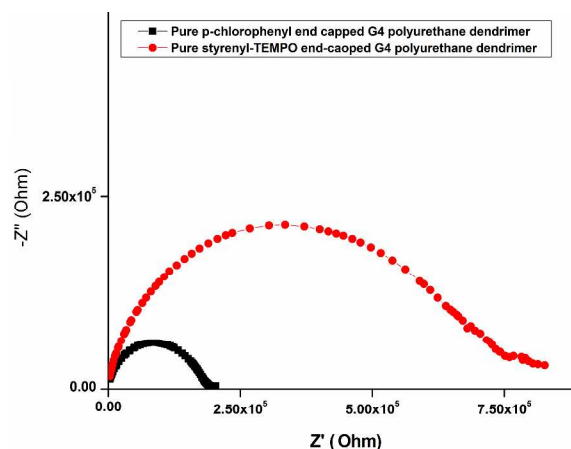


Fig. 5. Complex impedance plots of pure G4 polyurethane dendrimers.

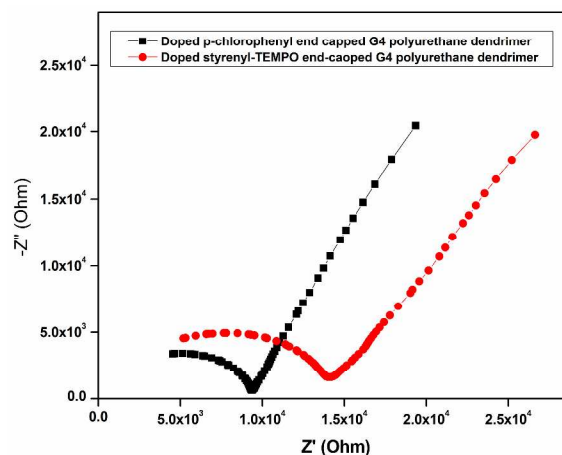


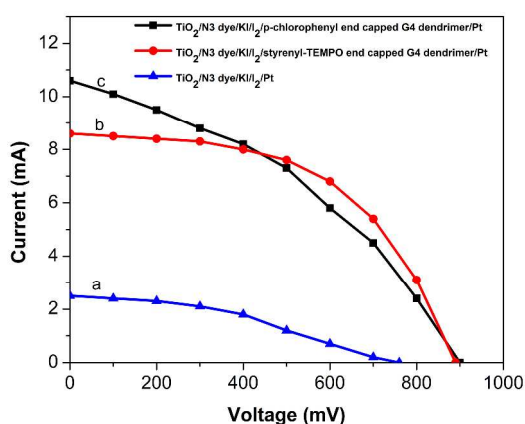
Fig. 6. Complex impedance plots of doped G4 polyurethane dendrimers.

Photovoltaic characterization of DSSCs.

Polymer-electrolyte based DSSCs are superior over liquid-electrolyte based DSSCs owing to the stability of the device and the elimination of the use of volatile solvents²³. For this study, two dendritic polyurethanes with identical skeleton but with different end groups were chosen. Both of the dendrimers are enriched with hetero atoms like nitrogen and oxygen, and the lone pairs of the electrons present in these atoms could readily interact with the metal cations added, that could increase the performance of the DSSCs. Figure 7 shows the I-V curves

Table 1. Ambient temperature electrical conductivity (σ_{298K}) values assessed for the un-doped and doped polymer electrolyte systems.

Electrolyte	Bulk Resistance (R_b) ($\times 10^4$ Ohms)	Conductivity σ ($\times 10^{-4}$ Scm $^{-1}$)
Pure <i>p</i> -chlorophenyl terminated G4 dendrimer	19	1.0
Pure styrenyl-TEMPO terminated G4 dendrimer	74	0.33
Doped <i>p</i> -chlorophenyl terminated G4 dendrimer	0.93	15
Doped styrenyl-TEMPO terminated G4 dendrimer	1.5	11

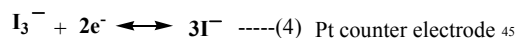
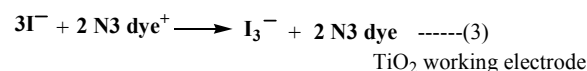
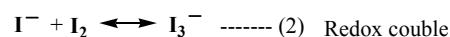
**Fig. 7.** Current-voltage characteristics of device based on (a) reference sample, (b) doped styrenyl-TEMPO terminated and (c) doped *p*-chlorophenyl terminated G4 polyurethane dendrimer at 50mW/cm 2 under AM 1.5 illumination.

recorded under the illumination of 50 mW/cm 2 at AM 1.5 solar irradiation for DSSCs fabricated with and without doped dendrimer electrolytes and the photovoltaic parameters obtained are given in Table 2. These results reveal that the devices based on doped G4 polyurethane dendrimer electrolytes exhibit remarkably better performance compared to that fabricated without the dendrimer. Moreover, the short-circuit current density (J_{sc}), the open-circuit voltage (V_{oc}), the fill factor (FF) and the photoelectric energy conversion efficiency (η) obtained for this work are significantly high compared to the reported work based on hyperbranched polyurethanes¹³. The photovoltaic parameters

Table 2. Photovoltaic parameters evaluated for G4 polyurethane dendrimer based dye-sensitized solar cell.

Sample Code	Open-circuit voltage V_{oc} (mV)	Short-circuit current density J_{sc} (mA/cm 2)	Fill factor (ff)	Efficiency η (%)
TiO $_2$ /N3 dye/KI/I $_2$ /Pt	760	2.5	0.40	1.5
TiO $_2$ /N3 dye/KI/I $_2$ / <i>p</i> -chlorophenyl terminated G4 dendrimer/Pt	900	10.6	0.51	9.7
TiO $_2$ /N3 dye/KI/I $_2$ /styrenyl-TEMPO terminated G4 dendrimer/Pt	890	8.6	0.53	8.1

of DSSC fabricated with styrenyl-TEMPO terminated dendrimer are slightly low compared to that obtained for *p*-chlorophenyl-terminated dendrimer. This is contradictory with the expectation and indicates that the charge transportation is relatively poor in the former case, and the same is favorably occur in the latter case from inner to periphery of the dendrimer owing to the electron withdrawing ability of the *p*-chlorophenyl group. The operational principle of DSSCs fabricated for this study is illustrated in Fig. 8. At first, the absorption of photon induces photoexcitation of the sensitizer (N3 dye) molecules, subsequently the N3 dye injects an electron into the conduction band of TiO $_2$ semiconductor. Here, the energy level of the N3 dye molecule must be above the conduction band of TiO $_2$ and the dye is regenerated by electron donation from the electrolyte containing I $^-$ /I $_3^-$ redox couple. Finally, the regeneration of the sensitizer (N3 dye) by iodide (I $^-$) ions intercepts the recapture of the TiO $_2$ conduction band electron by the oxidized dye (N3 dye). The triiodide (I $_3^-$) ions are then reduced to iodide (I $^-$) ions at the counter electrode and the electron flows through the external circuit and the circuit gets completed as given by the following equation.



Within the electrolyte system, metal cation (K $^+$) and iodide anion (I $^-$) are mainly coordinated with nitrogen atoms of polyurethane dendrimers by means of hopping mechanism which in turn paves the way for good ionic conduction as evidenced from Fig. 7. In addition, K $^+$ ions are bounded more rigidly and I $^-$ ions could be easily dissociated which facilitates electron transport by ion exchange referred to as a Grotthus-like exchange mechanism taking place between I $^-$ and I $_3^-$ ²⁴. On the other hand, I $^-$ /I $_3^-$ redox species in the blended dendrimer electrolyte enhances the kinetics of the dye regeneration reaction taking place in the cell. All these processes will favorably proceeded in the cell for the following reasons: (i) Dendrimer have large free volume between branch points spread over the molecule from inner core to peripheral end groups. This free volume will facilitate the charge transportation. (ii) Dendrimers are compact molecules owing to the globular shape. Due to the compactness and the inherent affinity of polyurethane dendrimers, they will have enhanced contact with TiO $_2$ electrode, thereby cell performance was improved.

Cite this: DOI: 10.1039/c0xx00000x

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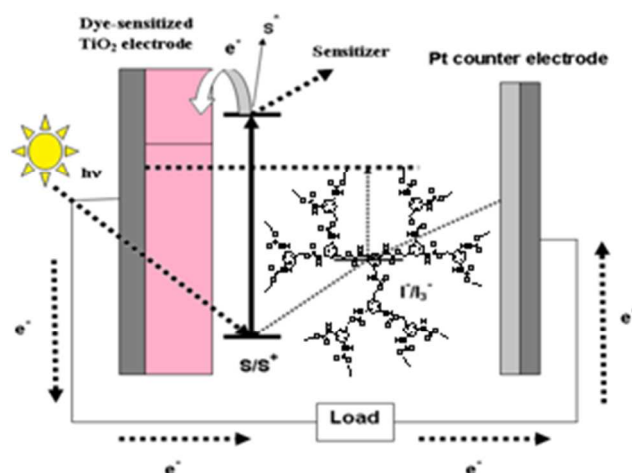


Fig 8. Schematic representation of the dendrimer based DSSC.

Conclusions

TiO₂ nanocrystalline DSSCs were fabricated using polyurethane dendrimers as electrolytes for the first time and found that the energy conversion efficiency of the cells was remarkably high compared to that fabricated without the dendrimer electrolytes. Among the two dendrimer electrolytes used, the one based on *p*-chlorophenyl-terminated G4 dendrimer shown high efficiency. Nitrogen atoms present in all the branch points of the dendrimers effectively interact with I⁻/I₃⁻ redox couple and enhances the ionic conductivity and energy conversion efficiency. The compact structure and dendritic topology are found to play a vital role in the improved performance of the cell.

Acknowledgement:

The authors thank the Department of Science of Technology, Government of India for financial support for this work (SERB Sanction Order No. and Date: SR/S1/PC-08/2010 (G).Dt. (13-07-2011). The authors also thank the National Centre for Nanoscience and Nanotechnology for the SEM facility.

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