

*Luminescence spectrometry* Measurements were performed by exciting the sample with a brief light pulse. The apparatus consists of a light source (laser LED) which excites the sample at 390 nm. The sample re-radiates, and the light is detected at a wavelength of 650 nm set by a mono-chromator. Signal from the excitation source begins to charge a capacitor within the time to amplitude converter (TAC). The fluorescence from the sample arrives at the photomultiplier tube at a later time, and stops the charging. The charge accumulated is converted directly into a potential difference and is now sent as a pulse to a multi channel analyser where it is allocated a channel related to its magnitude. This channel relates directly to a period of time. The signal from the TAC passes down standard coaxial cable of length 1-2 m and to the multichannel analyser (MCA), a PCI (personal computer interface) board with several available inputs, although only one is used in this experiment. Each voltage-amplitude is assigned with a particular channel of a certain time period. The software interface, Maestro 3.10 for Windows, plots a graph of time (x axis) against number of pulses (y axis), which can be plotted logarithmic. Spectrophotometer with laser excitation and micro-channel plate photo-multiplier detector provides an instrument response of 100 ps. The collected decay was in the microsecond range and the spectrum was fitted by Origin software with second order exponential decay. The average lifetime was calculated from the eq. 1, where  $A_i$  is the pre-exponential coefficient.

$$\tau = \frac{\sum_{i=1}^n A_i \tau_i}{\sum_{i=1}^n A_i} \quad (1)$$

*Film Preparation* TiO<sub>2</sub> solution was prepared by following the same procedure that has been described in the literature.<sup>1</sup> The UV, IR, CV studies of the dye absorbed on the TiO<sub>2</sub> semiconductor electrode were carried out on the ITO coated conducting glasses. The glass slides were washed with KOH ethanol solution and cut into 9 × 9 mm pieces which allows to be inserted into a 10 × 10 mm optical path length, quartz fluorescence cell. The TiO<sub>2</sub> solution was dispersed on the glass that was tightened by scotch tape at the four edges and rod over with a glass rod. The wet TiO<sub>2</sub>

electrode was dried in air for 15 min and then was sintered at 450 °C for 30 min. The electrode was immersed into the dye ethanol solution (typically 10<sup>-4</sup> M) when it was cooled down to 80 °C for 16 h. IR and UV was tested with a TiO<sub>2</sub> semiconductor electrode as the background. CV was carried out by using the semiconductor electrode as the working electrode, Pt wire as the counter and Ag / AgNO<sub>3</sub> (0.01 M in CH<sub>3</sub>CN) as the reference electrode. Nanocrystalline ZrO<sub>2</sub> solution and films were prepared by following the same method as that of TiO<sub>2</sub>.

*Solar cells* The general procedure for constructing the cell was similar to previously reported methods.<sup>2</sup> It is important to correct the IPCE for the light harvesting efficiency (see below), and then to correct for the absorption of the ITO and the electrolyte. The efficiency of the solar cell is often measured by the incident photon to current conversion efficiency (IPCE), the ratio of the number of electrons flowing through the external circuit to the number of incident photons. For a given area of cell the IPCE can then be expressed as follows:

$$\text{IPCE} = 1250 i_{\text{corrected}} (\mu\text{A}) / [\lambda (\text{nm}) P(\mu\text{W})] \quad (2)$$

Where  $I_{\text{corr}}$  is the dark-current corrected maximum (short-circuit) photocurrent at and P is the incident light intensity. Clearly, the IPCE is wavelength dependent and can be related to the light harvesting efficiency (LHE), which in turn is closely related to the absorption characteristics of the dye.

$$\text{IPCE}(\lambda) = \text{LHE}(\lambda) (\phi_{\text{inj}}) (\phi_{\text{eff}}) \quad (3)$$

Where  $A = 1000(\text{cm}^3 \text{L}^{-1}) \cdot \epsilon (\lambda) (\text{mol}^{-1} \text{L cm}^{-1}) \cdot \Gamma (\text{mol cm}^{-2})$ ,  $\phi_{\text{inj}}$  is the charge injection yield that depends on the lifetime ( $k_0$ ) and the injection rate ( $k_{\text{inj}}$ ) which depends on the excited state redox potential relative to the TiO<sub>2</sub> band edge and the coupling of the dye energy levels to the TiO<sub>2</sub> levels.  $\phi_{\text{inj}} = k_{\text{inj}} / (k_0 + k_{\text{inj}})$ .  $\phi_{\text{eff}}$  is the charge collection efficiency that depends on the structure and morphology of semiconductor layer. LHE measurements show that these cells have much larger

values than previous cells due to the greater coverage of dye, thanks in the main to the much greater surface area of the TiO<sub>2</sub> present. The maximum in the IPCE is measured at the  $\lambda_{\text{max}}$  of the IPCE curve. When the IPCE is integrated over the AM 1.5 solar spectrum, the result is related to the maximum power output of the cell  $(IV)_{\text{max}}$  which due to resistance effects will be smaller than product of  $I_{\text{max}}$  ( $=I_{\text{sc}}$ , the short-circuit current) and  $V_{\text{max}}$  ( $=V_{\text{oc}}$ , the open-circuit voltage) by a factor known as the fill-factor,  $f$ .<sup>3,4</sup> Solar cells constructed using the N3 dye have efficiencies of 10.4 % with  $I_{\text{sc}} = 18 \text{ mA cm}^{-2}$ ,  $V_{\text{oc}} = 0.72 \text{ V}$  and  $f = 0.73$ . The cell can operate for  $>10^7$  redox cycles, compared to  $10^4$  for organic dyes.