

# Light harvesting in silicon (111) surfaces using covalently attached protoporphyrin IX dyes

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Silicon photosensitisation using light harvesting structures represents an attractive solution for reducing the amount of semiconductor material.<sup>1-3</sup> Originally proposed by Dexter<sup>4</sup> silicon photosensitisation postulated the electron-hole pair generation via energy transfer from excited dye molecules on the silicon surface. This proposal opens the way for light harvesting and directed energy transfer for enhancement of the photo-excitation rate in indirect gap semiconductors.

In this work we investigate the potential of photosensitization of silicon surfaces using covalently attached protoporphyrin IX (PpIX) derivative molecules. The illuminated surface results in the interaction between the near field of the molecular dipole and the transition dipole moment of the electron transition between the valence and conduction band of the semiconductor. These 'anchored' organic molecules can assist in the design of an ultra-thin crystalline silicon cell which is simultaneously passivated and sensitized by an organic monolayer containing dye molecules (Fig. 1 and Fig. 2). In essence, it is possible to covalently attach organic molecules to the surface of a silicon crystal, allowing for the possibility of direct functionalisation of the crystal surface. Experimental verification of the near field interaction of dyes on surfaces has been carried out in the past by monitoring the fluorescence lifetime quenching near the surface.<sup>5-7</sup> We present time resolved fluorescence quenching measurements for dyes directly attached on the silicon surface (Fig. 3). In particular, we investigate the near field interaction of the excited dye at distances to the silicon surface less than 2nm (Fig. 4). We investigate the fluorescence quenching as a function of the PpIX-Si surface distance between 6Å-18Å using time correlated single photon counting. A diol linker molecule was used with a chain length that was varied from 2 carbon to 10 carbon lengths in order to change the distance of PpIX to the Si(111) surface. Reflection FT-IR and X-ray photoelectron spectroscopy verified the diol linker terminated Si(111) surfaces. A significant decrease in the fluorescence lifetime was observed at distances down to 6 Å due to energy transfer to silicon. We fit the experimental lifetimes to a classical model and predict up to 1000 times fluorescence quenching at such close distance to the Si(111) surface.

Light harvesting through photosensitisation of silicon opens the door to exciting new vistas for photovoltaics as it allows the separation of the photovoltaic process into two separate steps, an absorption step in the dye and a charge separation step in silicon. The material requirements for crystalline silicon can thus be reduced by several orders of magnitude.<sup>8-11</sup>

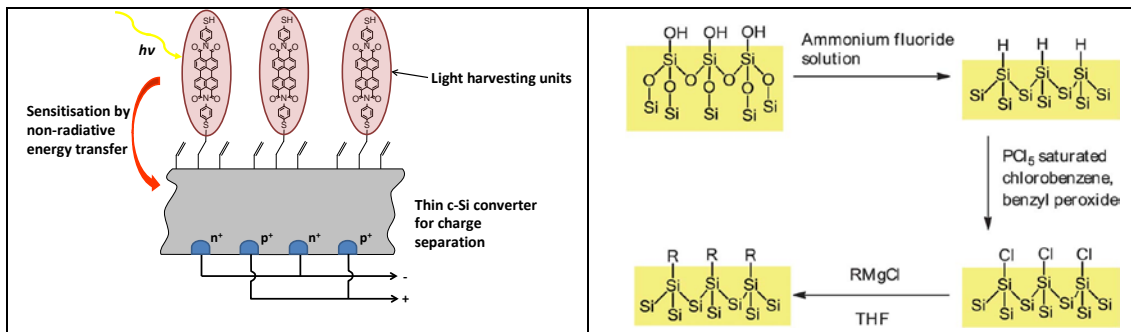


Fig. 1. Schematic diagram of a crystalline silicon solar cell sensitized by a light-harvesting structure on the surface.

Fig. 2. Synthesis route of alkyl monolayers on silicon surfaces.

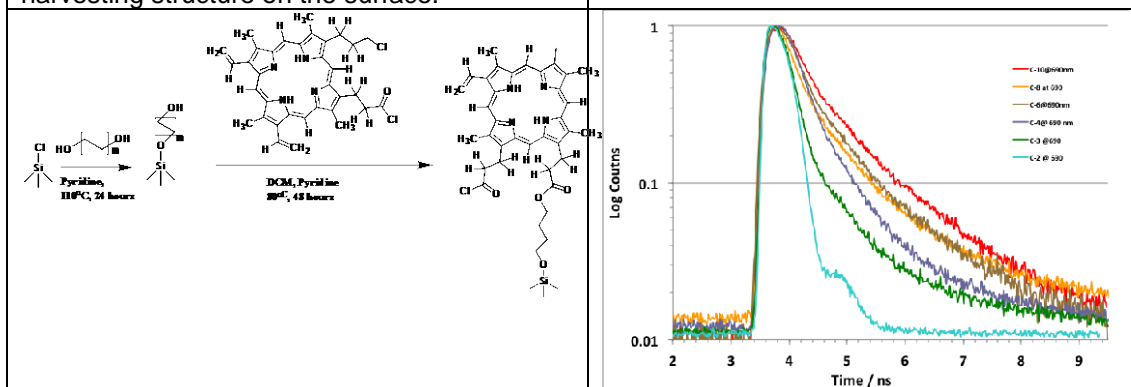


Fig. 3. Attachment of the acyl chloride porphyrin to the silicon surface. The linker (n) can be varied to modify the distance to the silicon surface between 0.6-1.8 nm.

Fig. 4. Observed fluorescence decay lifetime quenching of Porphyrin dyes directly attached to silicon surfaces as a function of the linker alkyl layer chain (n=2-10).

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