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

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We report the photosensitization of crystalline silicon via energy transfer using covalently attached protoporphyrin IX (PpIX) derivative molecules at different distances via changing the diol linker to the surface. The diol linker molecule chain length was varied from 2 carbon to 10 carbon lengths in order to change the distance of PpIX to the Si(111) surface between 6Å and 18Å. Fluorescence quenching as a function of the PpIX-Si surface distance showed a decrease in the fluorescence lifetime by almost two orders of magnitude at the closest separation. The experimental fluorescence lifetimes are explained theoretically by a classical Chance-Prock-Silbey model. At a separation below 2 nm, we observe for the first time, a Förster-like dipole-dipole energy transfer with a characteristic distance of R_o = 2.7 nm.

The term "light harvesting" is often used to describe a process which enhances the absorption cross section of the photosynthetic reaction complex by energy transfer, often called Förster resonance energy transfer (FRET).[1] It has been suggested on several occasions that a similar approach could be applied to semiconductors.[2–5] In the case of an indirect band gap material such as crystalline silicon, photosensitisation has the potential to substantially enhance the photoexcitation rate for electron-hole pairs, resulting in significant savings in material, and bringing about an exciting new paradigm for future solar cells and other optoelectronic devices.[6] Previous experimental studies have reported quenching of molecular fluorescence in proximity to silicon from evaporated dyes layers,[4,5,7] quantum dots,[8] Langmuir-

Blodgett (LB) films[9–12] or zeolite structures[13] but at a greater distance of the emitter from the surface of silicon (>2nm) than the work presented in this paper where we focus on emitter-surface separations of less than 2 nm. The native oxide present on the surface of silicon then needs to be removed and the silicon surface subsequently functionalised. This results in a well-prepared surface with careful control of the emitter-surface distance. Viewed more generally, the modification of the silicon surface via the direct covalent attachment of organic molecules has seen an intense activity[14–16] resulting in oxide free silicon surfaces (with molecules immobilised) with good stability and electronic (passivation) properties. Alkyl-modified silicon surfaces have received significant interest due to their potential applications in solar cells,[17,18] microelectronics,[19,20] biochemical sensing[21,22] and catalysis.[23]

In the present letter we report what we believe is the first demonstration of energy transfer at a controlled sub nanometer separation between a chromophore and silicon, which can be unequivocally attributed to near-field dipole-dipole interaction. A dipolar emitter placed within a subwavelength distance from the silicon surface "sees" an increased density of states into which radiation can be emitted, on account of coupling directly to the trapped modes in silicon via the evanescent field. Sometimes called "photon tunnelling", this mechanism explains well the increase of quenching rate at dipole separations of the order of a few tens of nanometers.[24] In contrast, the interaction at emitter-surface separations of the order of 1 nm which are under investigation in this paper is dominated by the near field interaction between the emitter dipole moment and the transition dipole moment of the electron-hole pair excited in silicon. This interaction is similar to the near field dipole interaction between molecules which gives rise to the Förster energy transfer. Also known resonance energy transfer, this mechanism is generally accepted as underpinning the light harvesting energy collection in photosynthesis. By changing the distance from the dye to silicon via the length of a linker molecule, allows the dependence of this energy transfer from

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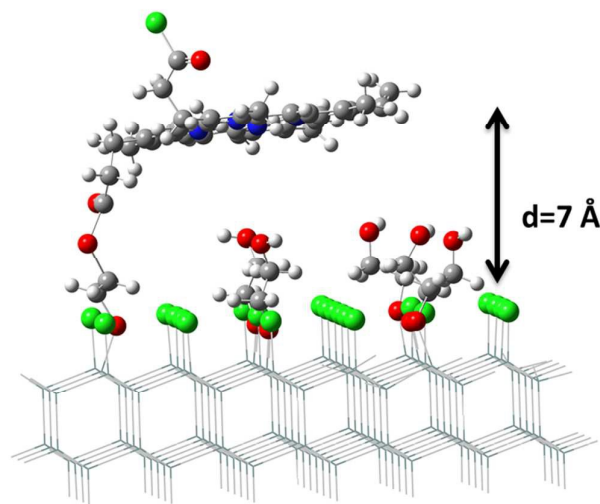
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Fig. 1 A molecular model of the silicon (111) surface with diols and a PpIX molecule covalently attached.

chromophore to semiconductor to be investigated in detail, and to separate the Förster-like energy transfer from photon tunnelling through the evanescent field.

The attachment of porphyrins to silicon surfaces has been well documented[25,26] and perhaps the closest example found for sensitizing silicon is reported in ref;[27] simpler experiments report the attachment of benzene or anthracene terminal groups[28] to a silicon alkyl monolayer by an esterification reaction, resulting in coverage of at least 70%. For the experiments performed in this paper, Protoporphyrin IX was chosen due to the commercial availability, ease of functionalisation and shifting of the absorption and emission maxima by coordination with metal ions. An example of a molecular model of a silicon (111) surface with ethane-diol linkers and a PpIX molecule attached is shown in Fig. 1. The presence of the large pi-ring will most likely force the molecule to adopt a parallel orientation with respect to the surface of silicon.

The first step towards attachment of PpIX was the addition of the appropriate diol linker (Table S1, ESI†) on the chlorine-terminated Si(111) surface (Scheme 1). By adding a small amount of base (such as pyridine), an increase in the uniformity of the siloxane monolayer is observed as well as a reduction in the required reaction temperature. FT-IR measurements on the resulting alcohol-terminated Si(111) surfaces confirmed the formation of the required monolayer, allowing subsequent functionalization of the alcohol chains (Fig. S4, ESI†). It was found empirically that to attach PpIX to the modified silicon surface successfully, pyridine should be added to the solution in order to catalyse and reduce the reaction temperature between the porphyrin and alcohol surface. This allowed a more gentle heating temperature of 80°C, reducing the chance of porphyrin decomposition. The resulting silicon surfaces with PpIX molecules attached were then washed with DCM to remove any physisorbed porphyrin, and allow further characterisation with FT-IR, XPS and fluorescence measurements. Reflection FT-IR and XPS verified the diol linker terminated Si(111) surfaces with estimated

coverages up to 30%. Subsequent functionalisation with PpIX molecules was verified with coverage of about 1-2%. The infrared spectrum of a 1,4 butanediol treated silicon surface after functionalisation with PpIX is shown in Fig. S3 and S5 (ESI†). The O-H peak of the functionalised surface is clearly visible, showing that unreacted alcohol groups remain. This is due to the much larger porphyrin group blocking unreacted surface sites. The various C-H groups of the porphyrin are
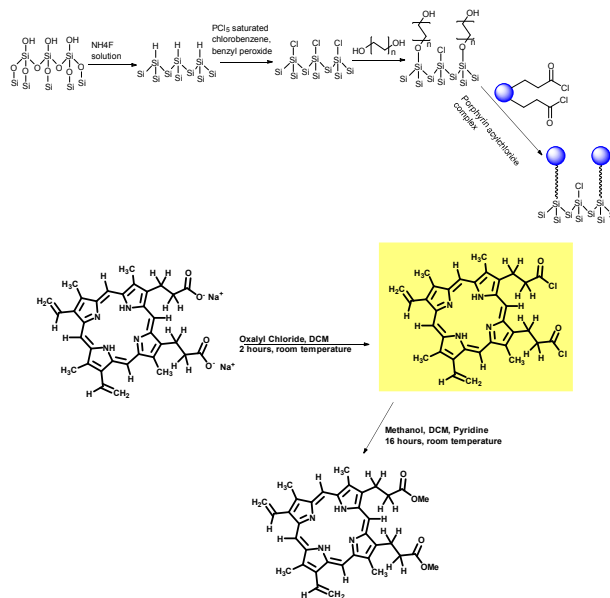
Scheme 1 Synthesis and attachment of the Protoporphyrin IX acyl chloride (PpIX-Cl) to the Si(111) surface.

clearly visible in the spectrum, as well as the CH_2 peak of the butanol-terminated surface and the ester C=O peak (Fig. S5, ESI†).

The presence of the porphyrin was further confirmed from XPS data. The nitrogen 1s binding region showed three distinct nitrogen binding energies; one for iminic nitrogen, another for pyrrolic nitrogen, and finally a smaller peak for possible physisorbed nitrogen, (Fig. S6, ESI†). The two peaks in the nitrogen 1s binding energy matched other literature data for porphyrins.[28] Interestingly, a 1:1 ratio of the integrals of the pyrrolic and iminic nitrogen peaks is not obtained as would be expected. This could suggest that a proportion of the surface-attached porphyrin has bound a transition metal ion within the porphyrin ring, reducing the number of pyrrolic nitrogen atoms observed. This metal could be incorporated during the porphyrin processing steps, arising from trace metal impurities found in all solvents. To confirm the correct assignment of the physisorbed nitrogen, a nitrogen 1s XPS spectrum was obtained for a 1,4-butanediol surface (Fig. S7, ESI†).

Variable Angle Spectroscopic Ellipsometry (VASE) measurement of the diol linker silicon surfaces and analysis confirmed the attachment of the diols linkers with different carbon chain lengths on the surface of silicon and were found in good agreement with DFT calculations (Table 1). The ellipsometric measurements were fitted to a simple Cauchy model (Fig S8, ESI†). Examples of steady state fluorescence

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spectra obtained from PpIX-functionalised (propane, butane and decane diol linker) silicon surfaces are shown in Fig. S9 (ESI†). To confirm that the spectrum was indeed due to the attachment of the porphyrin, a fluorescence spectrum of a 1,2-ethanediol terminated only surface was also obtained and showed no fluorescence activity. All PpIX attached silicon surfaces with different linkers showed similar steady state spectra and only the intensity of emission changed. The spectra do not show the typical two peaks for a PpIX in solution (Dimethyl ester)[29] occurring at 633 nm and 700 nm but instead show a broad emission peak starting from 610 nm to 800 nm with a maximum at 670 nm. This is to be expected for the broad bandwidth (16 nm) employed in order to measure sub-monolayer dye coverages. Normalised fluorescence decay curves of the various porphyrin-linked surfaces, together with decay fits are shown in Fig. 2.

Table 1 Variable Angle Spectroscopic Ellipsometry analysis results for the different Diol linkers on Silicon with different carbon chain lengths

| Carbon Chain Length	Sample	Measured Thickness (Å)	Calculated Thickness (Å)
2	Si(111)-O-CH$_2$-CH$_2$-OH	5.5 ± 0.6	6.0
3	Si(111)-O-CH$_2$-CH$_2$-CH$_2$-OH	9.5 ± 0.6	7.3
4	Si(111)-O-(CH$_2$-CH$_2$)$_2$-OH	14.4 ± 0.5	8.6
6	Si(111)-O-(CH$_2$-CH$_2$)$_3$-OH	15.0 ± 0.4	11.1
8	Si(111)-O-(CH$_2$-CH$_2$)$_4$-OH	17.2 ± 0.4	13.6
10	Si(111)-O-(CH$_2$-CH$_2$)$_5$-OH	18.5 ± 0.4	16.3

The fluorescence decay curves show that as the fluorophore is moved closer to the silicon surface, the fluorescence decay lifetimes become shorter indicating a greater degree of fluorescence quenching. The reason for the quenching of the fluorescence is likely to arise from energy transfer from the excited PpIX to silicon. As the distance between PpIX and the surface is reduced from 15 Å down to 5 Å the rate of energy
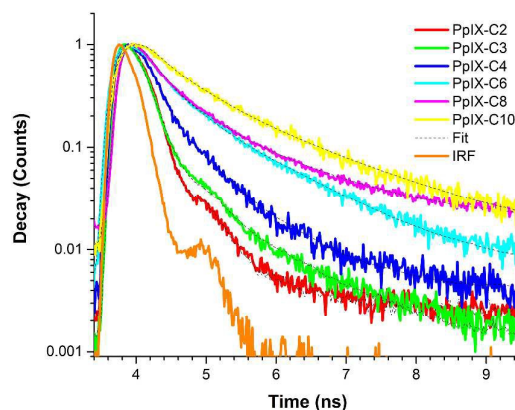
transfer becomes greater and the fluorescence lifetime decay shortens significantly. When the chromophore-surface distance becomes very small (such as for the ethanediol-linked PpIX), the decay almost matches the profile of the laser pulse reaching the resolution limit of the instrument (250 ps). As the linker chain-length is increased, the fluorescence decay time increases, although the largest differences in decay rates were between those for different shorter linker groups (Table S2, ESI†).

To describe the fluorescence quenching we have modified the classical theory by Chance, Prock and Silbey[30] (CPS) developed originally for the observation of fluorescence quenching of dye layers on the surface of metals. As can be seen in Table S2 (ESI†), the fluorescence lifetime increases with increasing distance to the surface. The fluorescence lifetime change is considerable, changing by almost two orders of magnitude when moving from ethanediol to decanediol-terminated surfaces, and the PpIX-silicon separation decreases from just below 2 nm to 0.6 nm. The fluorescence lifetime for the diol-linked PpIX-terminated surfaces is shown in Fig. 3. The red
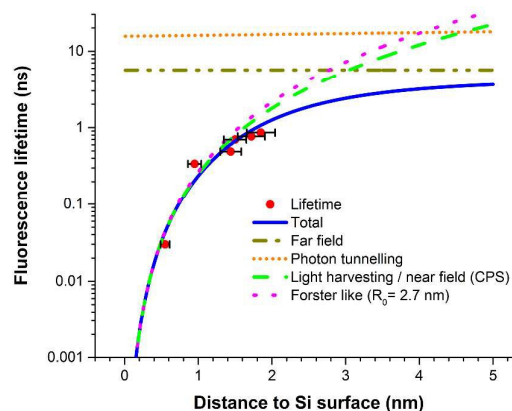
Fig. 3 The fluorescence lifetime for various diol linked porphyrin surfaces. Experimental points are fitted by Chance-Prock-Sibley theory (CPS, full blue line). Also shown, by dashed and dotted lines, are separate contributions from different mechanisms.

solid line in Fig. 3 was obtained by fitting the well-known CPS theory[30] using a fluorescence quantum yield of 0.2 which was close to reported value in literature.[31] We assumed, in keeping with theoretical understanding of electron transition in porphyrins, that the electric transition dipole moment is oriented in the plane of the molecule, parallel to the silicon surface. Other orientations, however, could also be used with little difference observed (Fig. S10, ESI†).

Fig. 3 shows different lifetime components for a dipole near the silicon surface, as modelled by the CPS theory. The far field contribution is simply the dipole emission in free space as modified by interference with a wave reflected from the surface. Photon tunnelling (studied in detail in ref. 16) is an optical effect describing energy transfer, through the evanescent field, from the excited molecular state directly to the photon states in silicon trapped by total internal reflection. Of principal interest is the near field component which

Fig. 2 The fluorescence decay curves of various chain-length terminated surfaces functionalised with protoporphyrin IX.

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corresponds to the interaction between the transition dipole moment at the molecule and at the excited electron-hole pair in silicon. The Förster-like energy transfer between an emitter dipole and an array of acceptors filling a semi-infinite half space is predicted to follow the distance dependence[1]

$$\frac{1}{\tau} = \frac{1}{\tau_o}\left(\frac{R_o}{d}\right)^3 \qquad\qquad (Eq.1)$$

where τ_o is the fluorescence lifetime in the absence of silicon interface, d is the chromophore-silicon separation and R_o is the equivalent of the Förster radius between molecules. We believe that the present work demonstrates for the first time, the Förster-like energy transfer between a molecule and semiconductor and allows the determination of the Förster radius R_o = 2.7 nm. Further work is needed to elucidate finer details of this interaction such as the role of direct and indirect transitions in the transfer[2] or the importance of screening at this small dipole-dipole separation.[6]

In conclusion, we have successfully attached a porphyrin dye to the silicon (111) surface by a siloxane/alcohol technique, as confirmed by infrared spectroscopy, XPS and fluorescence spectroscopy. By using terminal dihydroxyalkanes as the linker chain we have prepared a number of samples with controlled separations (ranging from 6 to 18Å) between the chromophore and the silicon surface. The silicon-chromophore separations determined by ellipsometry agree well with the calculated valued determined by DFT. The key quantity of interest - fluorescence quenching - agrees well with the predictions of the CPS model. In particular, at dipole separation from the silicon surface below 2 nm, we have identified unequivocally the dominant role of Förster-like resonance energy transfer, with a "Förster radius" of 2.7 nm. We believe that direct sensitisation of indirect bandgap semiconductors such as silicon has potentially a huge technological significance, turning, in effect, silicon into a direct-bandgap material.

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Silicon photosensitisation via FRET from Protoporphyrin dyes covalently attached on silicon (111) surface