

Electronic Supporting Information (ESI) for:

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

Nicholas Alderman^{1,2*‡}, Lefteris Danos^{3*}, Liping Fang⁴, Martin C. Grossel² and Tom Markvart^{1,5}

¹Solar Energy Laboratory, Faculty of Engineering and the Environment, University of Southampton, Southampton, SO17 1BJ, UK

²School of Chemistry, Faculty of Natural and Environmental Sciences, University of Southampton, Southampton, SO17 1BJ, UK

³Department of Chemistry, Energy Lancaster, Lancaster University, Lancaster, LA1 4YB, UK

[‡]Current Address: Department of Chemistry, University of Ottawa, Ottawa K1N 6N5, Canada

⁴Institute of Materials, China Academy of Engineering Physics, Mianyang, 621900, P. R. China

⁵ Centre for Advanced Photovoltaics, Czech Technical University, 166 27 Prague, Czech Republic.

* Corresponding Author: N.Alderman@soton.ac.uk

* Corresponding Author: L.Danos@lancaster.ac.uk

Experimental Details

Synthesis of 3,7,12,17-Tetramethyl-8,13-divinyl-2,18-porphinedipropoyl chloride: All porphyrin containing solutions were kept in darkness and under nitrogen. To a solution of protoporphyrin IX disodium salt (250 mg) in dry DCM (20 mL), 2.5 mL of a 2M solution of oxalyl chloride (0.7616 moles) was added and the solution stirred for 2 hours. After removal of the solvent under vacuum, the green powder was transferred to a glovebox for subsequent reactions.

To confirm the presence of the porphyrin acyl chloride, the product was reacted with methanol (5 mL) in DCM (10 mL), with the addition of pyridine (1 mL) for 16 hours at room temperature (Scheme 10.3). After removal of the solvent under vacuum, the red / purple solid was purified by column chromatography using a 1:10 methanol:DCM eluent. Two red compounds were obtained; the starting material and the di-methoxy porphyrin which was analysed. MS(ES-) m/z: 1181.6 (M_2^+), 591.3 (M^+), 454.2, 259.1, 170.1. 1H NMR (300 MHz, $CDCl_3$) δ ppm: 3.11-3.24 (4.37 H, 2xT), 3.50-3.67 (15.37 H, M), 4.25-4.35 (4.00 H, QN), 6.07-6.15 (2.03 H, T), 6.25-6.35 (1.89 H, T), 8.11-8.27 (2.07 H, M), 9.91-10.18 (4.00 H, M). (Fig. S1)

Mass Spectroscopy : Data was obtained on a Micromass ZMD electrospray MS and analysed using the Remote Analyser system. Fig. S2 shows the mass spectrum of the methoxy ester porphyrin synthesised via the acyl chloride protoporphyrin IX (PpIX-Cl).

Synthesis of Functionalised Silicon Surfaces: The silicon sample (10.5 x 10.5mm squares, n-type, 25 Ω cm^{-1} , 500 μm) was cleaned in a hydrogen peroxide in sulphuric acid (1:3, 45 minutes) solution, followed by a thorough rinse in de-ionised water. Once the sample had been thoroughly cleaned, the surface of the silicon was etched in semiconductor grade ammonium fluoride (degassed, 15 minutes) to remove the native oxide layer and hydrogen-terminate the surface. After drying under flowing nitrogen, the sample was passed into a nitrogen filled glovebox for functionalisation. The hydrogen-terminated silicon was immersed in a saturated solution of phosphorus pentachloride in chlorobenzene (110°C, 1.5 hours) to which a few grains (<1mg) of benzyl peroxide were added as a radical initiator. The sample was then washed in chlorobenzene and the appropriate 1,X diol (where X = carbon chain length). The chlorinated wafer was then immersed in the appropriate diol (10 mL) with 1 mL of pyridine and heated to 110°C for 24 hours. The structures of the different diols and PpIX derivative attached on Si(111) surfaces are shown in Table S1. After allowing the solution to cool and washing with methanol, the protoporphyrin IX acyl chloride (100 mg) in DCM (10 mL) was added in darkness with a few drops of pyridine at 80°C for 48 hours (Scheme 1). The sample was then sonicated with acetonitrile (10 x 5 mL) and dried under nitrogen, yielding the required surface.

Infrared Spectroscopy: Measurements were taken using a Bruker Tensor 27 spectrometer fitted with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector and a variable angle reflection accessory with polariser (VEEMAX II, PIKE technologies). For the measurements of the functionalised silicon samples, the reflection angle for the measurements was set to 37° with S-polarisation of the reflected beam; the scan count was set to 500 scans, with a resolution of 4 cm⁻¹ in the scan region 500 – 4000 cm⁻¹. For all samples, a background of the native oxide was recorded. In Fig. S3 to S5, the main bands visible at approximately ~3250 cm⁻¹ correspond to the O-H stretching vibration from the free diol linkers on the silicon surface. The bands at ~3072 cm⁻¹ and ~3018 cm⁻¹ corresponding to the vinyl H-C(=C) stretching absorption and the ~2970 cm⁻¹ and ~2946 cm⁻¹ peaks correspond to the antisymmetric and symmetric alkyl C-H vibrations. In Fig. S5 the ester carbonyl stretch is shown for the 1,4 butanediol PpIX molecule on the silicon surface at ~1740cm⁻¹. The observed splitting of almost equally intensity is due to the hydrogen bonding of adjacent vacant diol groups with the ester carbonyl group of the PpIX molecule. Our assignments are in agreement with previous reported literature on monolayers on porphyrins attached on silicon.^{1,2} The diol linker terminated Si(111) surfaces were estimated to have coverages up to 30%. The coverage decreased as a function of increasing diol linker due to steric hindrance, in accordance to previous reports in the literature.³⁻⁵ Subsequent functionalisation with PpIX molecules was verified with coverage of about 1-2%.

X-ray Photoelectron Spectroscopy: XPS measurements on the samples were performed on a Thermo Fisher ME17 Thetraprobe system with a monochromatic Al X-ray source, set to a 400 μm spot size. The scan count was set to 500 scans for the nitrogen spectra. Deconvolution of the spectra was performed by fitting the data to multiple Gaussian bands, reducing the residual square to a minimum. High resolution X-ray photoelectron spectroscopy (XPS) confirms the presence of protoporphyrin IX attachment on the silicon surface. The high resolution N 1s spectrum of the PpIX terminated silicon surface with a 1,4 butanediol linker is shown in Fig. S6, and the best fit was obtained with a three peak fit. From the integrals for the pyrrolic (-NH-) at ~400.6 eV and iminic (=N) at ~398.7 eV nitrogen peaks confirms that the PpIX molecules were attached on the surface in accordance with previous XPS spectra on porphyrins in the literature.^{2,6,7} It appears that some porphyrin groups have bound a metal atom. This is likely to have come from trace metal impurities present in the solvents used. The presence of the third peak N 1s at ~403 eV could be attributed to small amounts of physisorbed nitrogen or slight oxidation of the attached porphyrin molecule. A comparison of N 1s high resolution XPS spectra from a PpIX anchored silicon surface and a diol only linker silicon surface is shown in Fig. S7. To estimate the coverage of the porphyrin dye, the ratio of

nitrogen to oxygen in XPS was used assuming that nitrogen signals were only obtained from the dye, and oxygen signals only from the diol linker.

Quantum Mechanical Calculations: Density Functional Theory (DFT) calculations were carried out using the Gaussian 09 computational package employing the B3LYP exchange correlation energy functional and the 6-311G** basis set. The lengths of all the free molecules for this study were estimated from the optimised structures.

Variable Angle Spectroscopic Ellipsometry: The thickness of the organic thin film layers was measured with variable angle spectroscopic ellipsometry (VASE) from 250 nm to 1000 nm at three different incidence angles (60°, 65°, and 70°) using a spectroscopic phase modulated ellipsometer (M-2000 V Automated Angle, J. A. Woollam Co., Inc., USA). The data collected were analysed using a three-layer model (substrate/monolayer/air) using silicon for the substrate and a Cauchy model for the optical properties of the monolayer. The fitting of the ellipsometry parameters has followed standard procedures that have widely been reported in the literature for similar samples with organic monolayers attached on silicon surfaces.⁸⁻¹¹ The refractive index of the organic monolayer was restricted between 1.45-1.60 (550-1000nm), which is a typical value estimated for similar organic monolayers previously reported in the literature.¹²⁻¹⁴ The Si-H bare substrate was used as a reference and also to estimate the roughness of the surface. Multiple readings (on three different spots) were taken from each sample and averaged over all consistent measurements in order to minimise errors in the thickness measurements. There was no significant difference observed in the estimated organic layer thickness of the samples between the Protoporphyrin IX attached samples and diol linker only surfaces. The low coverage of the attached PpIX molecules on the silicon surface (1-2%) did not give appreciable change in the measurement of the thickness within the error of the measurement. In our case the angle of the monolayer to the surface does not affect the thickness within the 10% error that we have reported. Examples of ellipsometry model fits are shown in Fig. S8.

Time-Resolved Emission Spectra and Decays: Time-resolved emission spectra and decay measurements were carried out using time correlated single photon counting (TCSPC) setup on a FluoTime 200 (PicoQuant GmbH) system fitted with a 445 nm laser (LDH-P-C-445B, PicoQuant GmbH) with a variable repetition frequency range from 10-80 MHz driven, allowing a time domain range 12-100 ns for the fluorescence decay. The setup is equipped with a PicoHarp300 TCSPC board (PicoQuant GmbH) and a Hamamatsu photomultiplier (PMA-192) with a spectral range from 300 nm to 900 nm. The emission from the samples was collected at right angles to the excitation laser beam at 670 nm with a spectral bandwidth of 16 nm. The full width half maximum (FWHM) of the system's

instrument response function (IRF) was 175 ps. The fluorescence decay curves were analysed using the FluoFit software (PicoQuant GmbH, version 4.6.1) based on two-exponential models which involves an iterative re-convolution process.¹⁵ The quality of the fits was assessed by the value of the reduced χ^2 value (a value of less than 1.2 for an acceptable fit), and a visual inspection of the distribution of the weighted residuals and their autocorrelation function.¹⁶ To obtain the steady state fluorescence spectra from the samples, the fluorescence decay was measured at 2 nm intervals from 480 to 750 nm. After measuring the decay at each point for 15 seconds, the emission spectrum can be obtained by plotting the maximum intensity at each wavelength.

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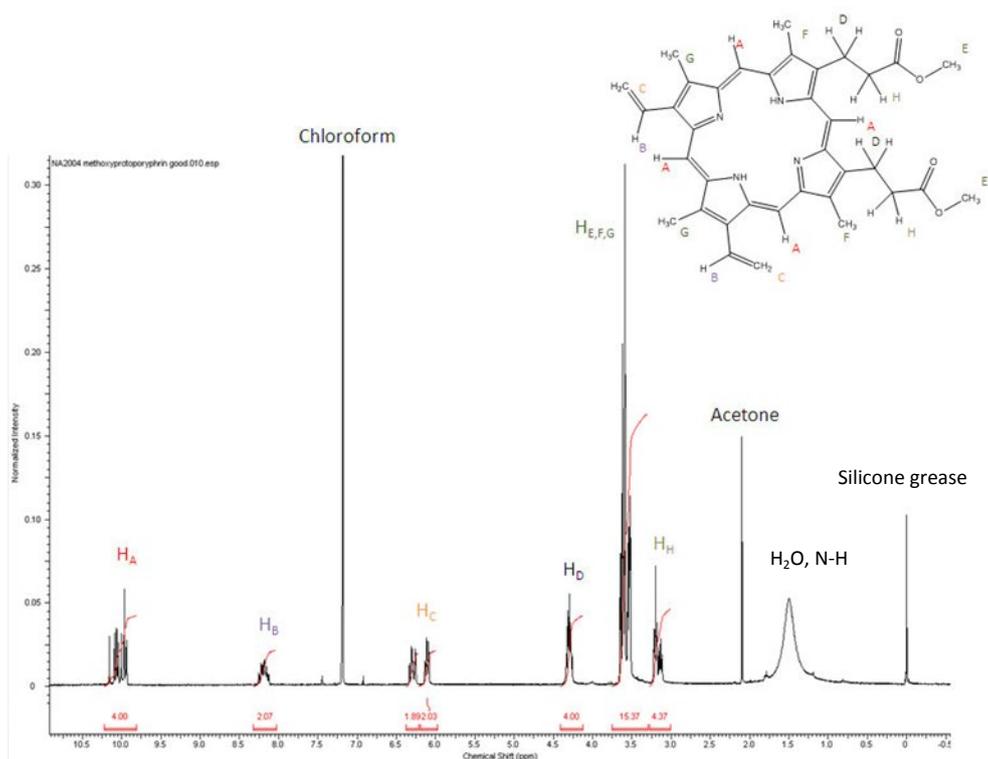


Fig. S1 ^1H NMR spectrum of the methoxy ester porphyrin synthesised via the acyl chloride protoporphyrin IX (PpIX-Cl).

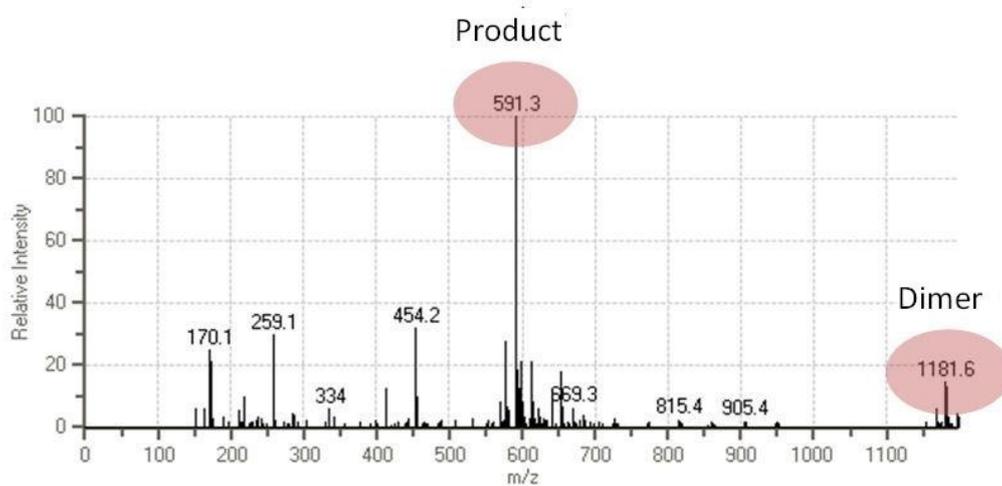


Fig. S2 Mass spectrum of the methoxy ester porphyrin synthesised via the acyl chloride protoporphyrin IX (PpIX-Cl), showing a parent ion peak for the product and a peak for the dimer of the product.

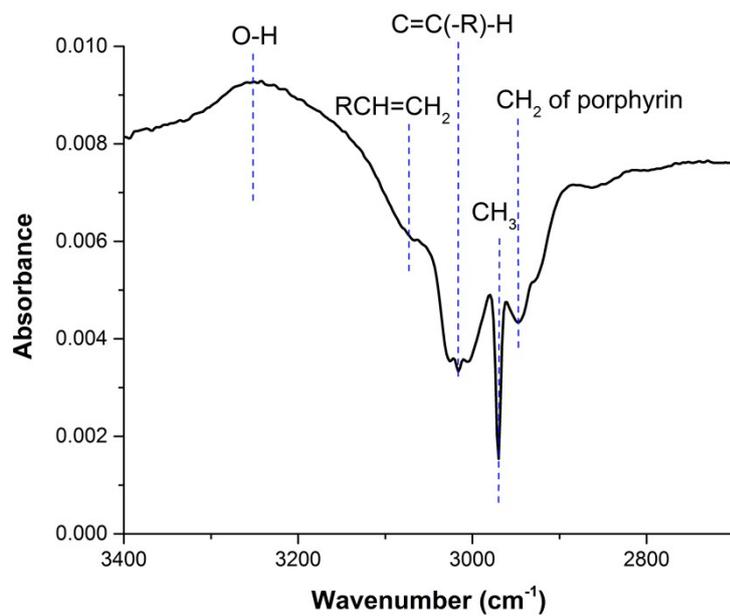


Fig. S3 FT-IR spectrum of the O-H and C-H stretching region for a 1,4 butanediol-PpIX terminated Si(111) surface.

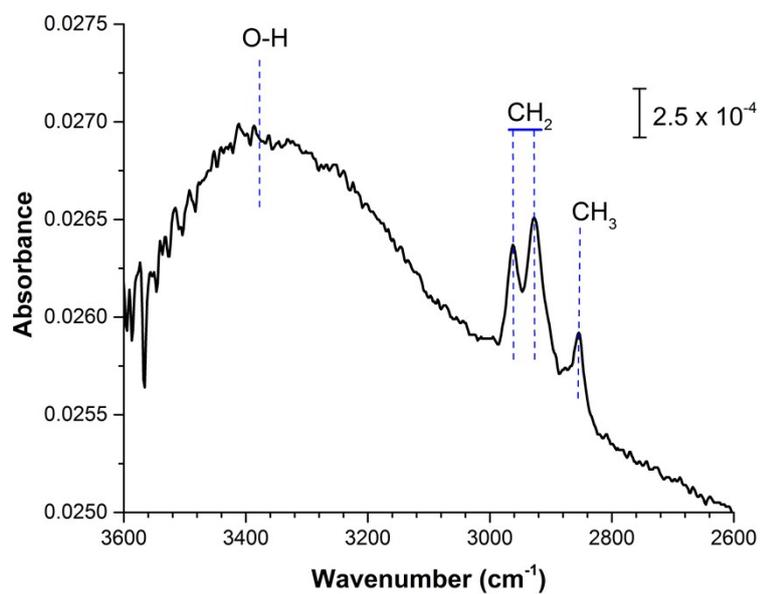


Fig. S4 FT-IR spectrum of the O-H and C-H stretching region for a 1,4 butanediol only terminated Si(111) surface.

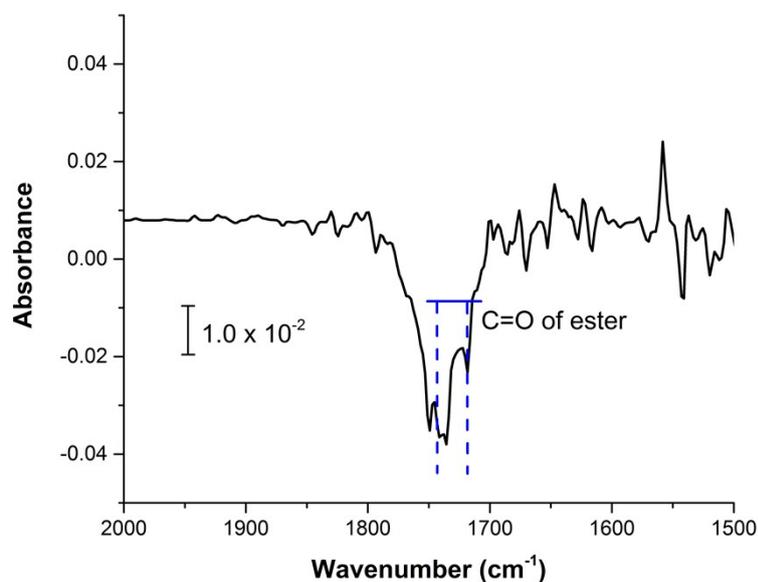


Fig. S5 FT-IR spectrum of the C=O stretching region for a 1,4 butanediol-PpIX terminated Si(111) surface.

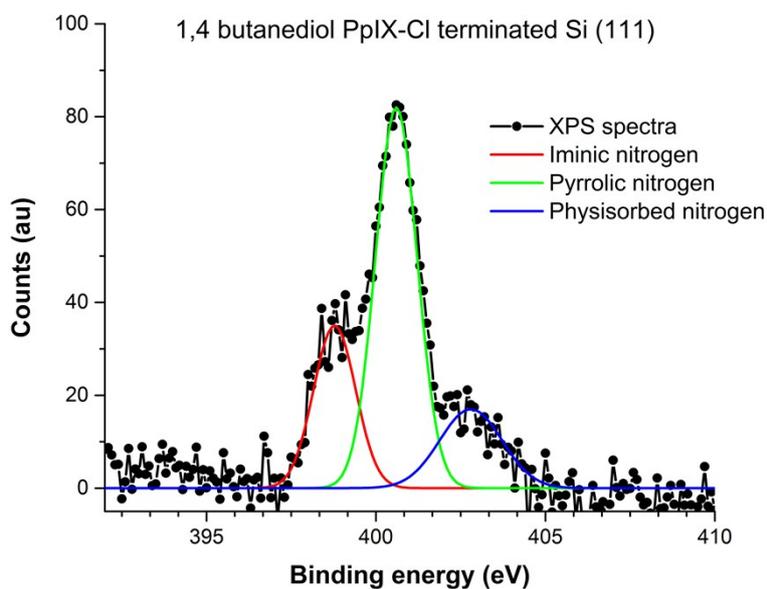


Fig. S6 High-resolution XPS spectrum in the N 1s binding region for a 1,4 butanediol-PpIX terminated Si (111) surface. The line + symbol indicate the experimental data and the solid lines indicate the fitted curves.

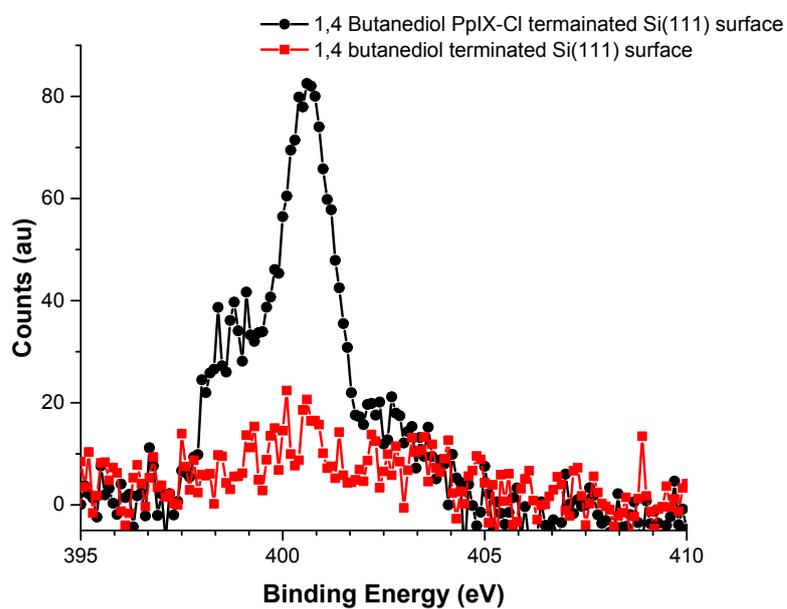


Fig. S7 High-resolution XPS spectrum in the N 1s binding region for a 1,4 butanediol-PplX terminated Si(111) surface and a 1,4 butanediol only terminated Si(111) surface.

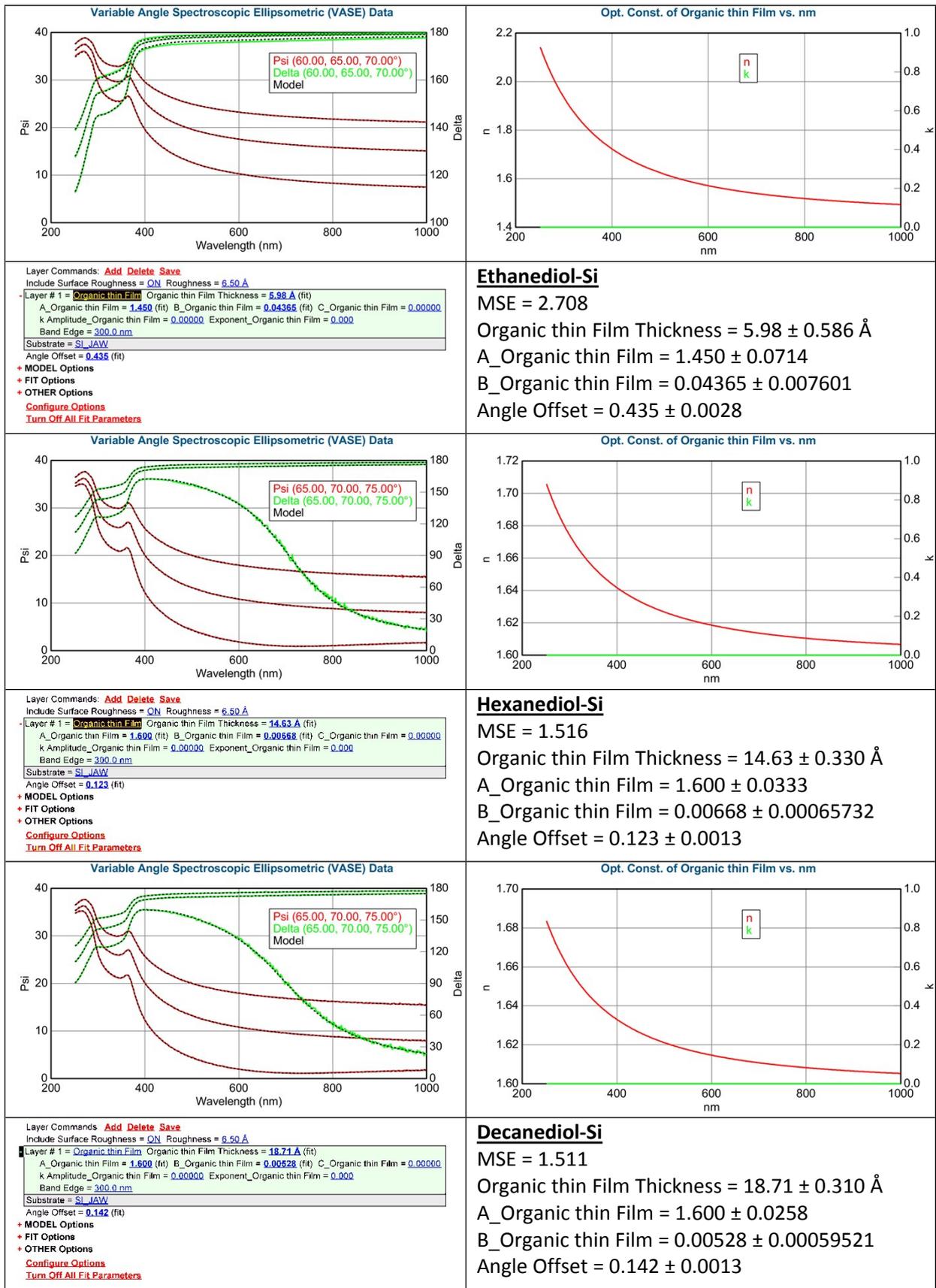


Fig. S8 Examples of ellipsometric measurements and model fits for ethanediol, hexanediol and decanediol terminated Si(111) surfaces.

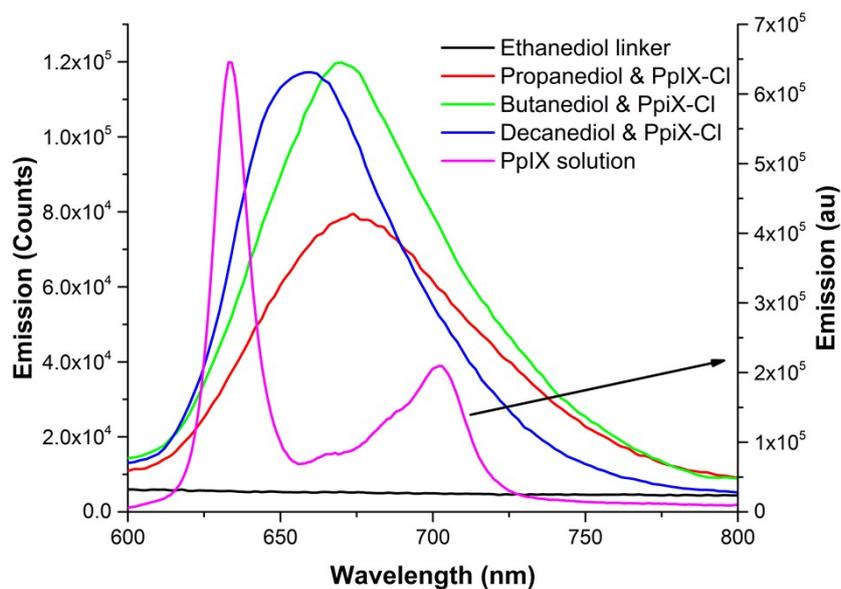


Fig. S9 Emission spectra of PpIX in solution, propanediol, butanediol and decanediol PpIX terminated Si(111) surfaces together with an ethanediol only terminated Si(111) surface.

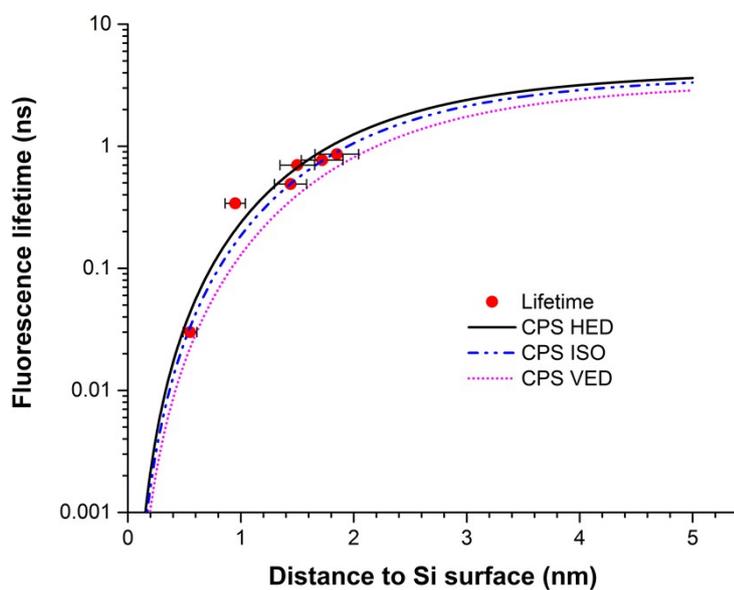


Fig. S10 Normalised rate fit of the CPS theory for horizontal (HED), isotropic (ISO) and vertical (VED) emission transition dipole moment orientations of the chromophore with respect to the surface of silicon. The experimental points (in blue) are shown together with the fitted lines.

List of Tables

Table S1 The names and structures of the diols and protoporphyrin molecules used to produce the Si(111) terminated surfaces in this study.

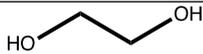
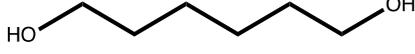
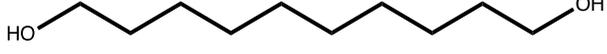
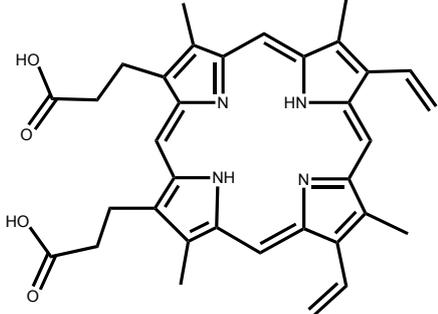
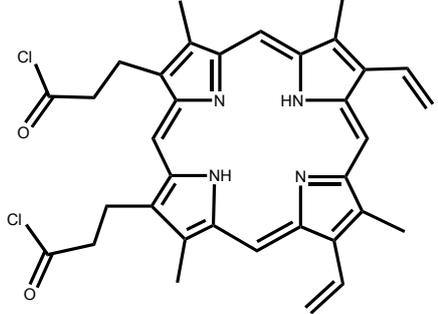
Name	Sample	Structure
1,2-Ethandiol	HO-CH ₂ -CH ₂ -OH	
1,3-Propanediol	HO-CH ₂ -CH ₂ -CH ₂ -OH	
1,4-Butanediol	HO-(CH ₂ -CH ₂) ₂ -OH	
1,6-Hexanediol	HO-(CH ₂ -CH ₂) ₃ -OH	
1,8-Octanediol	HO-(CH ₂ -CH ₂) ₄ -OH	
1,10-Decanediol	HO-(CH ₂ -CH ₂) ₅ -OH	
Protoporphyrin IX (PpIX)		
Protoporphyrin IX Chloride derivative	(PpIX-Cl)	

Table S2 Decay lifetimes for the various diol-PpIX terminated silicon surfaces.

Sample	Measured Lifetime (ns)
Si(111)-O-CH ₂ -CH ₂ -O-PpIX-Cl	0.03 ± 0.003
Si(111)-O-CH ₂ -CH ₂ -CH ₂ -O-PpIX-Cl	0.34 ± 0.02
Si(111)-O-(CH ₂ -CH ₂) ₂ -O-PpIX-Cl	0.49 ± 0.04
Si(111)-O-(CH ₂ -CH ₂) ₃ -O-PpIX-Cl	0.70 ± 0.05
Si(111)-O-(CH ₂ -CH ₂) ₄ -O-PpIX-Cl	0.77 ± 0.05
Si(111)-O-(CH ₂ -CH ₂) ₅ -O-PpIX-Cl	0.86 ± 0.06