Electronic Supplementary Material (ESI) for Chemical Communications.
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Supporting Information

Experimental

All chemicals and solvents were purchased from Sigma-Aldrich. Preparation of complexes **Eu.1** (Figure 2) was carried out as described previously, [1] characterisation data for the novel complex **Tb.1** are reported here. Modification of glass interfaces (cleaned using hot piranha solution prior to modification) was undertaken by spin coating 100 µl of 20 mM aryl azide in anhydrous DMF at 1000 rpm for 30 seconds. The samples were irradiated for 30 minutes at 365 nm. After irradiation the interfaces were sonicated in anhydrous DMF for five minutes, prior to drying under a stream of N_2 (g) and analysis.

X-ray-photoelectron spectroscopy was undertaken using a VG Escalab II spectrometer employing Aluminium Kalpha radiation (1486.6 eV) and a hemispherical analyser for detection of electrons. The Pass Energy was set at 50 eV for survey scan of the sample, and 20 eV for the more intense scans of specific areas. The resulting spectra were analysed using CasaXPS peak fitting software, and sample charging corrected using C 1s as a reference setting at 285.0 eV.

All luminescence measurements were carried out using a Cary Eclipse fluorescence spectrophotometer. A delay time of 0.1 ms was used to remove scattered light and residual fluorescence. Unless stated otherwise, emission spectra were collected with excitation and emission slit widths of 20 and 5 nm respectively; while for excitation spectra excitation and emission slit widths of 5 and 20 nm respectively were used. The effect of atmosphere on the emission spectra was investigated by degassing, with N_2, an airtight cuvette, containing a modified glass substrate at angle of 45 ° to the corners of the cuvette, and recording spectra. The cuvette was then opened to the atmosphere and a second emission spectrum was recorded. The ratiometric oxygen response was calculated using:

$$\left(\frac{I_{546}}{I_{616}}\right)_x \div \left(\frac{I_{546}}{I_{616}}\right)_{max} \qquad (1)$$

where I_{546} and I_{616} give the terbium and europium responses, respectively; and x denotes the atmosphere (N_2, air, etc.) in which the relative ratiometric response is being calculated. The analytical curve was constructed by preparing atmospheres containing varying percentages of oxygen, with the response calculated as described by equation 1. This was done as has been reported previously by controlling the relative flow rates of oxygen and nitrogen into the cuvette using the method reported. [2]

Tb.1

^{1}H NMR (500 MHz; D_2O, pD7): δ 299.8, 274.8, 257.9, 254.7, 220.8, 203.9, 186.6, 132.4, 124.6, 107.9, 105.4, -77.1, -82.3, -94.2, -96.3, -98.9, -103.6, -138.8, -152.1, -156.6, -179.8, -247.8, -337.2, -357.9, -426.1, -433.6. Only resolved peaks outside -20 to 20 ppm are reported. LR-ESMS: *m/z* calc. for $[M+H]^+$ 662.14, found 662.17. IR-ATR (cm^{-1}): 2103 (N_3), 1587 (C=O). UV-Vis: λ_{max}: 329 nm. Luminescence lifetimes: H_2O: 0.32 ms, D_2O: 0.87 ms.

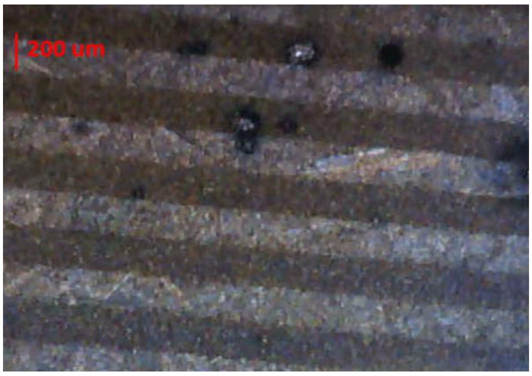
Photografting of Azidoaniline

Contact angles - SI 1 summarises the contact angles, and associated controls, for the grafting of **AA** to glass substrates. A higher contact angle, compared to the controls (no irradiation undertaken) was observed upon photografting. This is indicative of the formation of a hydrophobic organic film at the interface, stable to extended sonication, as a result of irradiation, and consistent with previous reports of the photografting of aryl azides to hydroxyl terminated interfaces via generation of a reactive nitrene species.[3, 4]

SI 1. Contact angles of 4-Azidoaniline photografted on glass. A more hydrophobic surface results from irradiation, indicating the formation of a stable film upon UV irradiation.

Concentration (mM)	UV exposure	Contact angle (°)	Error (°)
20	No	12	3
20	Yes	21	5
200	Yes	35	6

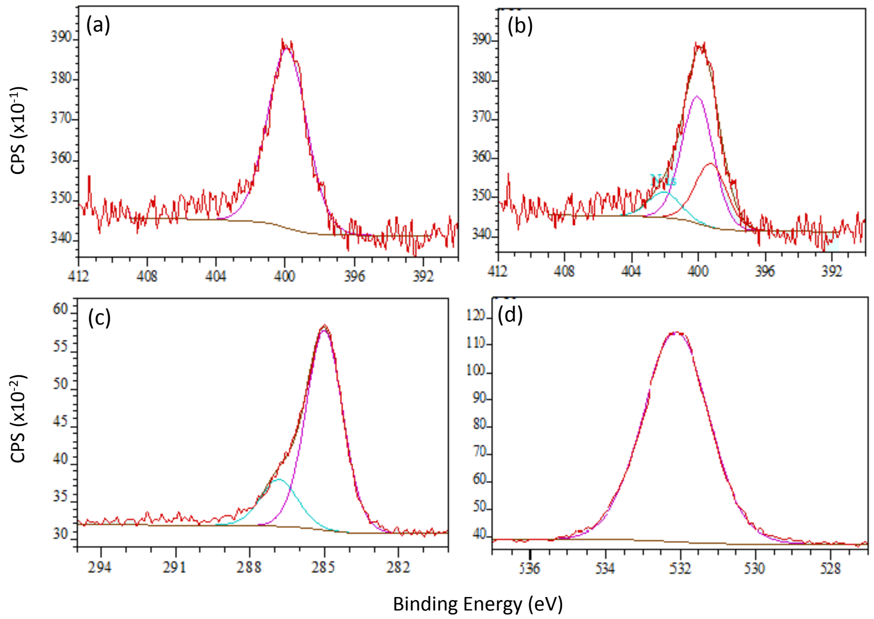
Condensation figures further confirmed the selective photografting of **AA** at oxide terminated interfaces (in this case silicon). Patterns of **AA** films were prepared by placing a photomask with 200 µm lines over the substrate during irradiating. The condensation figure (SI 2) show areas of higher hydrophilicity where the mask covered the substrate, and hence, demonstrates spatially resolved modification of the substrate. This further underlines the role of nitrene generation, by irradiation of the azide, in the formation of a stable film.



SI 2. Condensation figure of **AA** patterned on a silicon substrate using a photomask with 200 µm line features during irradiation.

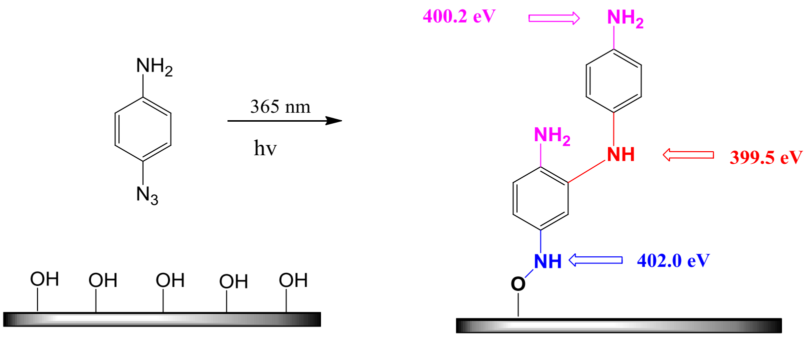
Ellipsometry - Equivalent films on silicon gave ellipsometric film thickness of 1.2 ± 0.3 nm, indicative of a layer one to two aryl groups thick. The results are consistent with those of previous workers who have reported the formation of multilayers films upon photografting or aryl azides;[3, 5] and correlate well with the XPS fitting (see below) which indicate a primary amine signal one to two times that of the secondary amines, suggesting the formation of relatively thin multilayers between one and two aryl groups thick.

XPS - SI 3 shows narrow scans of the N 1s (a and b) C 1s (c) and O 1s (d) of glass modified by spin coating a 50 mM solution of **AA** followed by UV irradiation. Photografting results in the appearance of a strong N 1s signal (a and b), while virtually no N 1s signals were observed in the absence of irradiation (not shown) with the physiorbed films easily removed upon sonication.



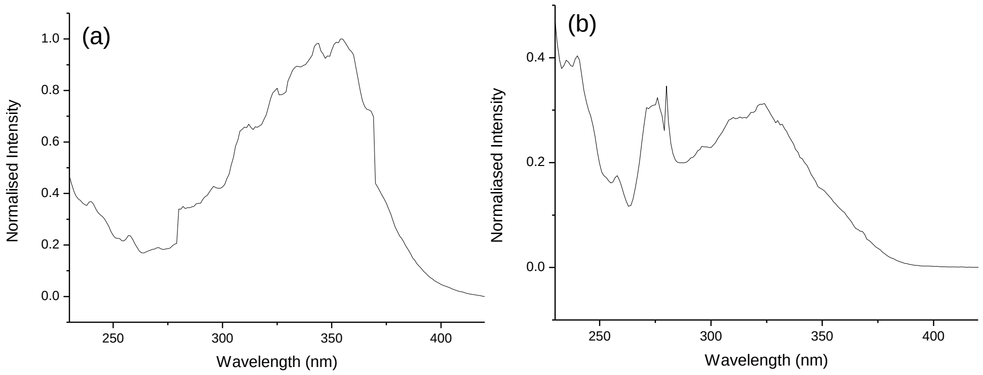
SI 3. Narrow scans of the N 1s (a and b) C 1s (c) and O 1s regions of aniline modified glass. After peak fitting figures b, c and d all have fitted peaks of the same FWHM (2.1 eV) while the fit of a single nitrogen environment (a) gives a FWHM of 2.7 eV, indicating the presence of multiple nitrogen environments as shown in (b).

Comparison of the full-width half-maximum (FWHM) of the nitrogen signal to that of the proximate C 1s and O 1s signals can give valuable information concerning the number of nitrogen environments in the film. The FWHM of the C1s and O 1s peaks (SI 3 c and d respectively) of 2.1 eV indicates that the fit of a single nitrogen environment (Figure 2 a, FWHM = 2.7 eV) is not viable. However, a fit of three environments gives a plausible FWHM of 2.1 eV, as shown in Figure 2 b. The peaks at 399.5, 400.2 and 402.0 eV can be assigned to secondary amine, primary amine and NHO-X nitrogen environments respectively. Secondary amine groups are expected to result from insertion of photo-generated nitrines into C-H bond of adjacent molecules, while primary amine groups are present as a result of the aniline functionalities. The NHO-X environment may be attributed the presence of covalent grafting to the interface resulting in N-O bonds (SI 4).[6]



SI 4. Proposed structure of Azidoaniline derived films on oxide terminated interfaces. The secondary amine groups, which result from nitrene C-H bond insertion, are observed through Nitrogen 1s signal at 399.5 eV. Primary anline nitrogens are observed at 400.2 eV. Aryl surface bonds result from nitrene insertion into O-H bonds, with the corresponding nitrogen 1s region at 402 eV.

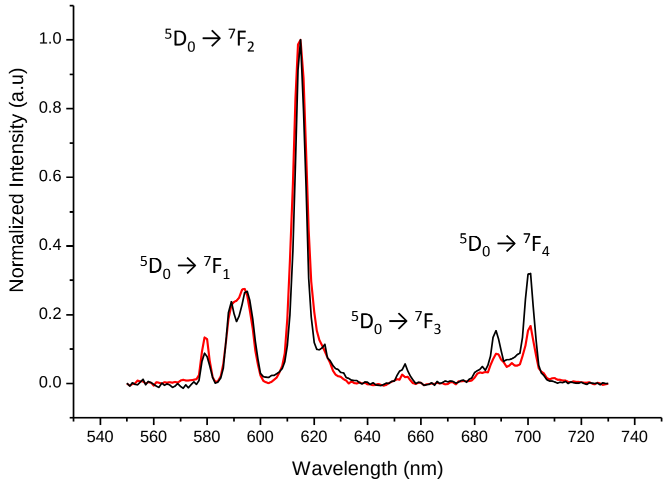
Excitation Spectra



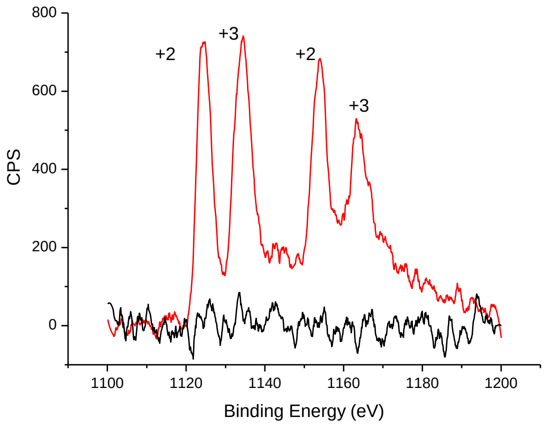
SI 5. Excitation spectra of (a) Eu.1 (λe_m = 616 nm) and (b) Tb.1 (λ_{em} = 546 nm) derived films.

Characterisation of Eu.1 derived films

Comparison of the intensities $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ with the $^5D_0 \rightarrow {}^7F_4$ for the solution and surface bound species shows a significant change in environment around the lanthanide center, ascribed to the reaction of the azide during photografting.



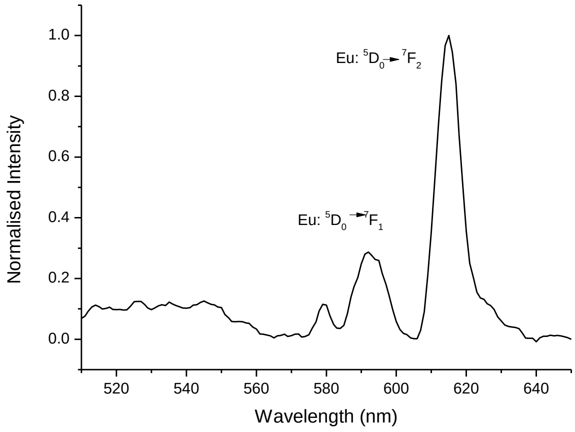
SI 6. Normalised emission spectra (λ_{ex} = 350 nm) of EuDO3A modified glass substrate (red) and of EuDO3A in H_2O (black).



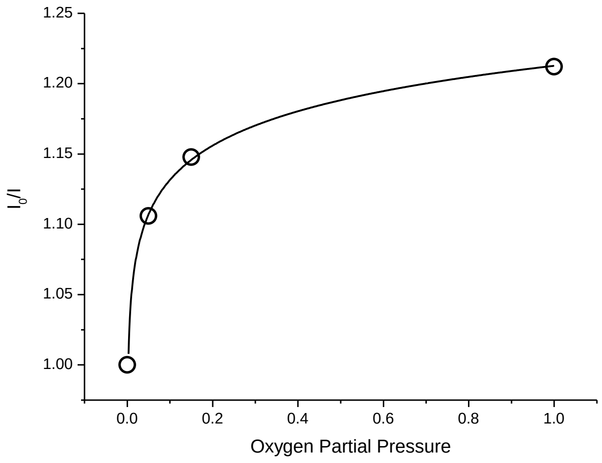
SI 7. XPS spectra of photo-grafted **Eu.1** complex on glass (red) and the corresponding control where no UV irradiation was undertaken (black). Europium is seen in the +2 and +3 oxidation state.[7]

Luminescence of mixed Ln.1 films

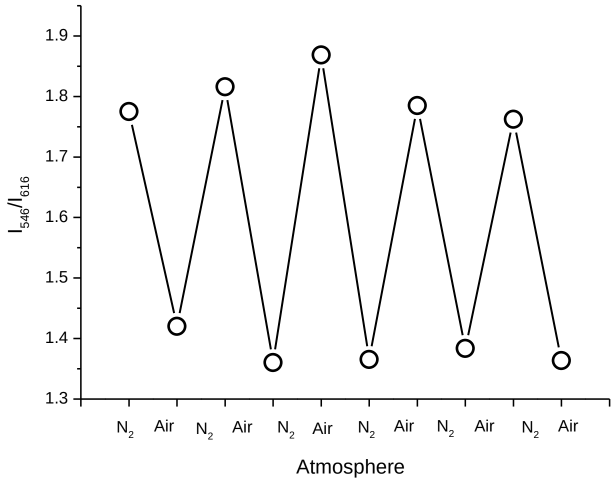
Mixed **Ln.1** films were prepared by pin coating a mixture of 10 mM **Tb.1** and 10 mM **Eu.1** onto quartz substrate and carrying out photografting as described in the experimental. The resulting luminescence spectrum (λ_{ex} = 350 nm) is shown in Figure SI 8. The europium $^5D_0 \rightarrow {}^7F_n$ signals are observed whereas the terbium $^5D_4 \rightarrow {}^7F_n$ responses are absent.



SI 8. Luminescence emission spectrum (λ_{ex} = 350 nm) of a mixed **Tb.1** and **Eu.1** film.



SI 9. Stern Volmer plot for the Tb $^5D_4 \rightarrow ^7F_5$ response. The nonlinear response is attributed to heterogeneity is the system as has been observed before for surface bound systems and is based on variable microenvironments in which the luminophores reside.[8]



SI 10. Non-normalised reversibility of oxygen switching data from figure 4b

References

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