Supporting Information

Experimental

All chemicals and reagents were purchased from Sigma Aldrich, unless specified otherwise. **Eu.1** was synthesised as described previously.[1] Gold substrates were prepared by thermal deposition of 100 nm of gold on Si (100) substrates (Silicon Materials) using a 5 nm chromium adhesion layer. All aqueous solutions were prepared from 18.2 Ω Millipore water. Prior to use gold substrates were cleaned by immersion in piranha solution (a 3:1 by volume mixture of 18 M sulphuric acid and 30% hydrogen peroxide) for 15 seconds and washed with copious amounts of (18.2 Ω Millipore) water, prior to drying under a stream of N_2 (g).

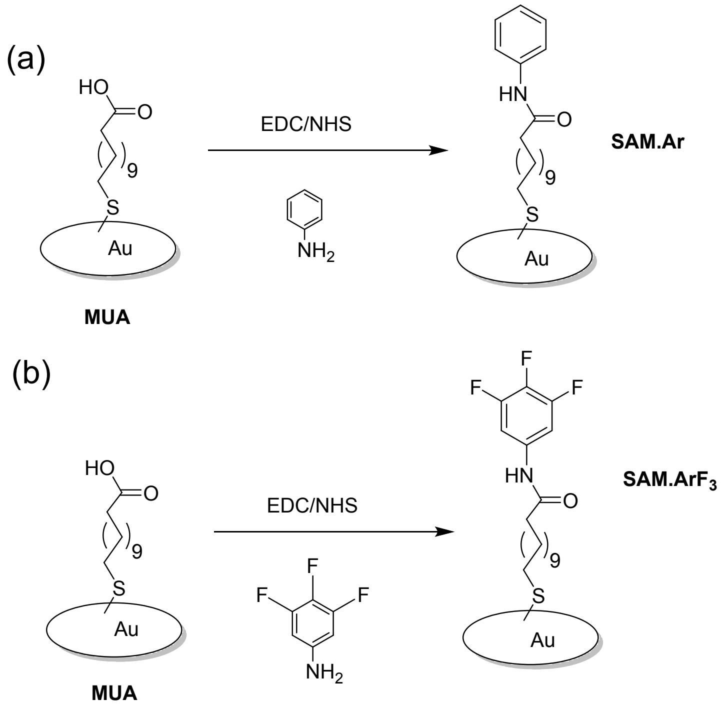
Ferrocene terminated self-assembled monolayers (**SAM.Fc**) were formed by immersing gold substrates in 1 mM 11-(Ferrocenyl)undecanethiol (95%) in ethanol for 24 hours, after which time they were removed and washed with copious amounts of ethanol prior to analysis and azide photografting. Benzene (**SAM.Ar**) and trifluorobenzene (**SAM.ArF$_3$**) interfaces were constructed by first preparing carboxylic acid terminated films by immersion of gold substrates in a 1 mM solution 11-mercaptoundecanoic acid (MUA) in ethanol for 24 hours. Subsequently the substrates were activated by immersion in a aqueous solution 0.4 M ethyl(dimethylaminopropyl) carbodiimide and 0.1 M N-Hydroxysuccinimide (NHS) for 40 minutes prior to transferring to a 10 mM solution of the hydrochloride salt of either aniline or trifluoroaniline in dimethylformamide for 24 hours. Controls were prepared by immersion of the MUA monolayers in aniline without prior activation (see SI. 1 for reaction scheme).

Photografting was undertaken by spin coating a 20 mM solution of **Eu.1** in methanol onto the SAM primer layers at 1000 rpm for 30 seconds. The interfaces were left in the dark until residual methanol had evaporated (10 mins) prior to 20 mins irradiation at 365 nm. After photografting the interfaces were sonicated in methanol for 3 mins to remove any loosely bound physisorbed material. Control interfaces were prepared for which no irradiation was undertaken, with the interface instead stored in the dark for 20 mins prior to post-modification sonication.

Ellipsometry was undertaken as described previously[2] employing a Beaglehole Instruments Picometer Ellipsometer, with a refractive index of 1.45 assumed for the organic layer on the underling gold substrate. Stated ellipsometric film thicknesses are an average of six measurements over three samples, two measurements per sample. The errors are given as two standard deviations of the average. 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 20 eV. 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 undertaken on Cary Eclipse fluorescence spectrophotometer. Excitation and emission slit widths of 20 nm and 5 nm, respectively, were used. All luminescence measurements were carried out following excitation at 350 nm using a delay time of 0.1 milliseconds and a gate time of 2 ms to minimise interference from short lived fluorophores and scattering effects and maximise the observed signal. All electrochemistry was carried out using a Ecochemie type II µAutolab. Spectro-electrochemistry was undertaken in four window quartz cuvette incorporating a photo-switchable gold substrate or control working electrode (prepared as described above) a platinum mesh counter electrode and a silver wire reference (used due to space restrictions within the spectroelectrochemical cell). Spectroelectrochemical measurements were undertaken in anhydrous acetonitrile (ACN) containing 0.15 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) electrolyte. An excitation wavelength of 350 nm was used. Switching was carried out between 0 and 0.7 V vs Ag wire. Cyclic voltammograms were recorded under the same conditions.

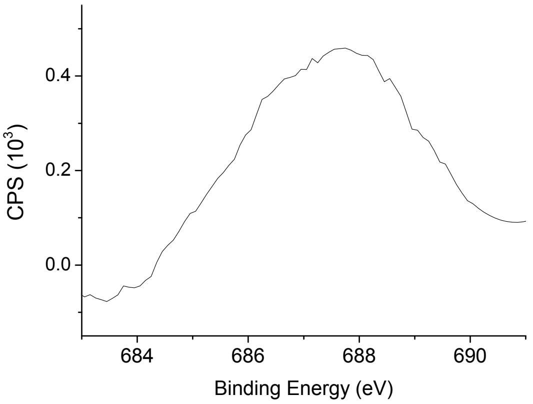
Preparation of benzene and trifluorobenzene terminated SAMs (SAM.Ar and SAM.ArF$_3$)

Control interfaces were prepared as outlined in SI 1. Initially carboxy terminated films were prepared by immersion of gold substrates in 11-mercaptoundecanoic acid (MUA) for 24 hours. Subsequently the interfaces were activated by immersion in a aqueous solution containing 0.4 M ethyl(dimethylaminopropyl) carbodiimide and 0.1 M N-hydroxysuccinimide (NHS) and then transferred to a solution of the relevant aromatic amine (either aniline or 3,4,5 triflouroaniline) in DMF for 24 hours. The **SAM.Ar** and **SAM.ArF$_3$** films exhibited ellipsometric thicknesses of 2.0 ± 0.3 and 1.9 ± 0.1 nm, respectively. Immersion of MUA terminated interfaces in aniline without prior activation lead to film thicknesses of 1.2 ± 0.2 nm, consistent with previously reports[3] for MUA layers on gold, and indicative of the covalent coupling of the aromatic amines to the MUA film only after activation.



SI 1. Schematic describing the preparation of **SAM.Ar** and **SAM.ArF$_3$** control interfaces

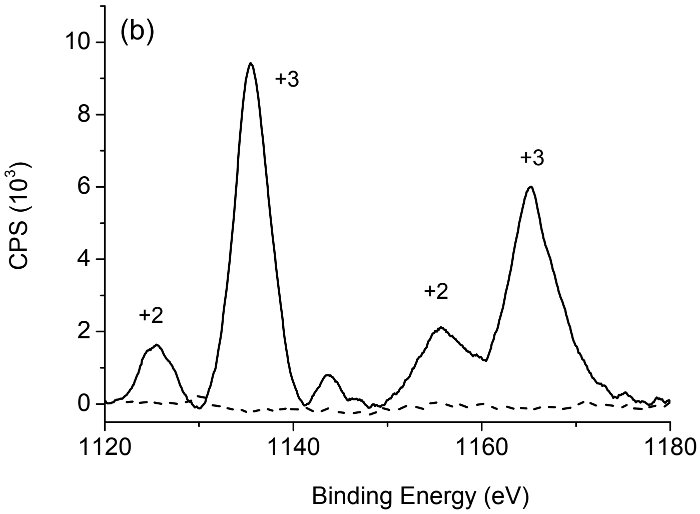
X ray photoelectron spectroscopy revealed the F 1s signal for the SAM.ArF$_3$ interfaces, as seen in figure SI 2 below.



SI 2. XPS F 1s spectrum of the SAM.ArF$_3$ interfaces.

XPS of SAM.Fc.Eu Film

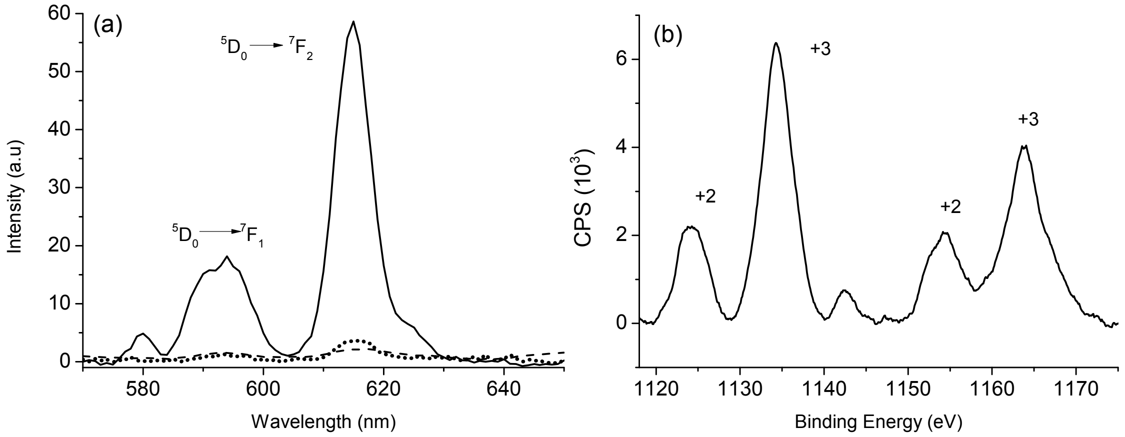
Europium 3d XPS spectra of **SAM.Fc** interfaces after deposition of **Eu.1** with (—) and without (---) irradiation prior to post grafting sonication, show a stable europium layer is only formed after nitrene generation after irradiation. Note: XPS analyses revealed europium primarily in the expected +3 oxidation state, with significantly smaller quantities in the europium +2 oxidation state, as assigned previously.[4]



SI 3. XPS spectra showing narrow scan of the europium 3d regions of the photografted **SAM.Fc** interfaces (—) and corresponding control (---).

Luminescence and XPS spectra of SAM.Ar and SAM.ArF$_3$ derived interfaces

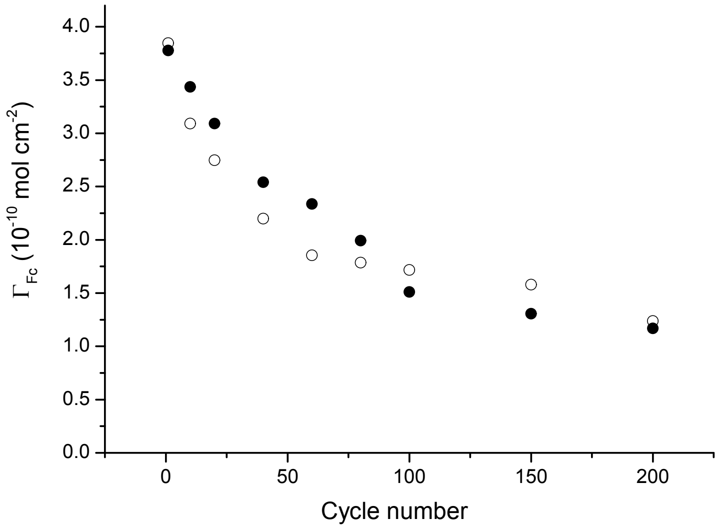
Emission spectra (λ_{ex} = 350 nm) non ferrocene incorporating europium interface (**SAM.Ar.Eu,** —) are shown in SI 4. After photografting the fingerprint europium emission was observed; however on the corresponding control (deposition of **Eu.1** on **SAM.Ar** but no irradiation) no europium emission signal was observed (---). Attempted photografting of **Eu.1** into **SAM.ArF$_3$** interfaces proved unsuccessful with only negligible europium emission observed (•••). This expected observation is attributed to the inert nature of the C-F bonds.



SI 4. (a) Emission phosphorescence (delay time = 0.1 ms) spectra λ_{ex} = 350 nm of **SAM.Ar.Eu** (—) and **SAM.ArF$_3$** (•••) interfaces after photografting of **Eu.1.** Control for **SAM.Ar (---)** prepared by the same method except no exposure to light to induce photografting was undertaken. (b) XPS spectra showing narrow scan of the europium 3d regions of the photo-grafted interfaces **SAM.Ar.Eu.**

Electrochemical cycling of SAM.Fc.Eu Interfaces

SAM.Fc.Eu interfaces were cycled in 0.15 M TBAPF$_6$ in acetonitrile at 0.1 V s^{-1} and the ferrocene surface concentration determined as a function of cycle number by integration of the redox couple charge



SI 5. Ferrocene surface concentration vs cycle number in 0.15 M TBAPF$_6$ in acetonitrile at 0.1 V s^{-1} for **SAM.Fc.Eu** interfaces. The surface area was defined using a 008 kalrez O-ring and the surface roughness (actual area/ geometric area) determined using Fe(CN)$_6^{3-/4-}$ and a Randles–Sevcik formula to be 1.5.

The drop in ferrocene electro-activity is of the same order of magnitude as the drop in switchable europium emission (25-50 %) when analyses consider the respective timeframes associated with the ferrocenium oxidation state.

References

1. M. Tropiano and S. Faulkner, *Chem, Commun*, 2014, **50**, 4696.
2. J. Lehr, J. Bennett, M. Tropiano, T. J. Sorensen, S. Faulkner, P. D. Beer and J. J. Davis, *Langmuir*, 2013, **29**, 1475.
3. S. M. Mendoza, I. Arfaoui, S. Zanarini, F. Paolucci and P. Rudolf, *Langmuir*, 2007, **23**, 582.
4. D. Li, X. Zhang, L. Jin and D. Yang, *Opt. Express*, 2010, **18**, 27191.