

A General Preparative Route to Self-assembled Monolayer Surfaces of Polypyridine Ligands and their Metal Complexes†

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The *in situ* reaction of 4-methylpyridine, 5,6-dimethyl-1,10-phenanthroline, 4,4'-dimethyl-2,2'-bipyridine, or *fac*-Re(4,4'-dmbpy)(CO)₃Cl with self-assembled surfaces derived from BrCH₂[CH₂]_nSi(X)₃ (*n* = 2 or 7; X = Cl or OMe) in the presence of the strong base lithium diisopropylamide gives new films incorporating the ligands or Re complex.

Self-assembled monolayer and multilayer structures containing specific structural motifs, chromophoric groups or redox-active centres are important in such diverse applications as catalysis, photoimaging and sensor technology. Thin films of self-assembled organosilane monolayers and multilayers are ideal for such studies since their chemistry is highly developed.¹ Previous synthetic strategies for the surface attachment of redox centres or chromophores have focused principally on three general methods; (i) the pre-synthesis of the target molecule, for example, an appropriate substituted organothiol for self-assembly on Au surfaces,² (ii) the coupling of a surface-attached monolayer to a molecular grouping *via* an amide or ester linkage,³ and (iii) reaction of a surface-confined nucleophile with a carbocation.⁴

Here we describe a general preparative route to monolayers of pyridinic ligands on SiO₂ (fused silica) and give examples of preparations of metal complexes, using Re^I chemistry as the specific example. Our method, which relies on the direct reaction of a carbanion derived from a methyl-substituted pyridine or polypyridine ligand⁵ with a preformed bromoalkylsilane surface, results in the creation of a hydrocarbon tether to the surface. This is notable since the stability of this linkage should be greater than that of hydrolytically sensitive amide or ester linkages or redox-sensitive ether or amine linkages.

A typical surface preparation is as follows. Prior to coating, 1 cm × 5 cm quartz plates were soaked in a 1:1 mixture of 30% H₂O₂ and concentrated H₂SO₄ for at least 5 h after which

time the plates were repeatedly rinsed in distilled water followed by drying at 110 °C for several hours. Silanization, according to a method known to give monolayers of silane,⁶ was accomplished in a glovebox containing a N₂ atmosphere using a 'dipping apparatus' that accommodated up to 5 plates. For 3-bromopropyltrimethoxysilane, the dipping apparatus was filled with 35 ml of freshly distilled toluene and *ca.* 50 μl of the silane (*ca.* 0.1% by volume) followed by stirring of the solution for *ca.* 10 min. The whole assembly was then taken out of the glovebox, 1 drop of glacial HOAc was added, the solution mixed, and the preparation was heated to 60 °C for 1 h. After heating, the plates were extensively washed with toluene and baked in an oven at 110 °C for 5 min. For 8-bromooctyltrichlorosilane a similar procedure was used.

For ligand attachment, the bromoalkylsilane plate was transferred to the glovebox where it was exposed to a solution of the heterocycle (*ca.* 10 mg in 25 ml of 2 mol dm⁻³ LDA solution in heptane-tetrahydrofuran-ethylbenzene). Typically, the plates treated in this manner were soaked in this solution for 20 min, but it was found that 10 min and 2 h exposure gave the same UV-VIS spectrum. The plates then were extensively washed with toluene, soaked and washed with methylene chloride, and soaked and washed in absolute MeOH. Essentially the same procedure can be used in the case of *fac*-Re(4,4'-dmbpy)(CO)₃Cl to provide a simple, single-step procedure to attach the Re-bpy chromophore as [*fac*-Cl(CO)₃Re(4-Me-bpy-4'-(CH₂)₄-(Si)-)] I [note that we will adopt a nomenclature involving -(Si)- to designate surface attachment].

Characterization of a surface preparation was accomplished by contact angle measurements, UV-VIS absorption spectroscopy and emission spectroscopy in addition to the charac-

† Abbreviations used: py = pyridine; 4,4'-dmbpy = 4,4'-dimethyl-2,2'-bipyridine; LDA = lithium diisopropylamide.

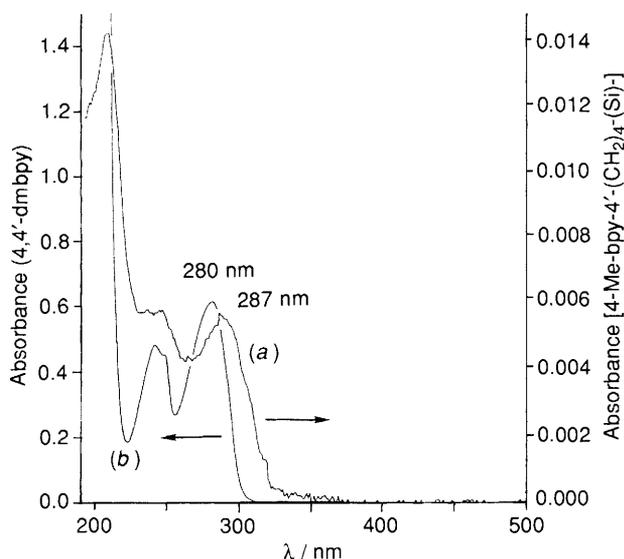


Fig. 1 Absorption spectra in the UV region for (a) [4-Me-bpy-4'-(CH₂)₄-(Si)-] **II** (287 nm maximum for the low-energy transition measured at the air-film interface and (b) 4,4'-dmbpy (280 nm maximum measured in MeCN)

Table 1 Estimated surface coverages and contact angles

Surface functionality ^a	Surface coverage/mol cm ^{-2b}	Contact angle ^c
Fused silica (acid washed)	— ^d	30°
-(Si)-Ph	1.2 × 10 ⁻⁹	89°
-(Si)-(CH ₂) ₃ Br	— ^d	64°
-(Si)-(CH ₂) ₂ (py)	1.3 × 10 ⁻⁹	61°
[-(Si)-(CH ₂) ₂ (pyH)] ⁺ Cl ⁻	— ^d	27°
-(Si)-(CH ₂) ₄ (py)	4.8 × 10 ⁻¹⁰	53°
-(Si)-(CH ₂) ₄ (Mebpy)	2.0 × 10 ⁻¹⁰	70°
-(Si)-(CH ₂) ₄ (Mephen)Re(CO) ₃ Cl	— ^d	69°
-(Si)-(CH ₂) ₄ (Mebpy)Re(CO) ₃ Cl	1.8 × 10 ⁻¹⁰	69°

^a -(Si)- denotes the surface siloxane linkages. ^b Estimated by UV-VIS spectroscopy; see text. ^c Advancing angle (H₂O). ^d Not measured.

teristic chemical reactions discussed later. An example is shown in Fig. 1 where the absorption spectrum of [4-Me-bpy-4'-(CH₂)₄-(Si)-] **II** and the solution model 4,4'-dmbpy are compared. Although overall similarities prevail, the surface spectrum is broadened and shifted to lower energy than that of the model. Table 1 shows the calculated surface coverage values for the pyridinic ligands and Re complexes based on the electronic spectral transitions for the solution models. For the calculations, the solution ϵ_{max} values were assumed to be invariant in order to provide an approximation to the two-dimensional surface extinction coefficients (ϵ_s). For example, the surface coverage of bipyridine sites (Γ_{bpy}) in a typical preparation is estimated to be ca. $2\text{--}2.5 \times 10^{-10}$ mol cm⁻² by using $\epsilon_{s,280}$ as 1.41×10^7 cm² mol⁻¹ (using the lowest energy $\pi\text{--}\pi^*$ transition of the model complex 4,4'-dmbpy). Inspection of the Γ values listed in Table 1 reveals interesting trends in the number of surface sites. For example, if direct silanization is conducted with 4-py(CH₂)₂SiCl₃ to produce 4-py(CH₂)₂-(Si)-**III** the resulting surface has a Γ_{py} value of 1.3×10^{-9} mol cm⁻², which falls in the range of a typically accepted figure for surface silanol sites on acid-washed silica⁷ of 6.7×10^{-10} to 1.9×10^{-9} mol cm⁻². Surprisingly, the surface coverage for a LDA-4-Mepy reaction with Br(CH₂)₃-(Si)-**IV** was found to be 4.8×10^{-10} mol cm⁻² which appears to be a case of submonolayer coverage. We are currently pursuing methods by which the extent of surface

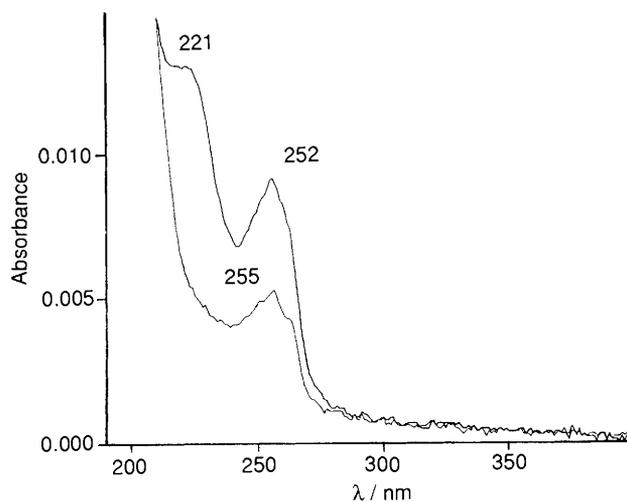


Fig. 2 Absorption spectra in the UV region for 4-py(CH₂)₂-(Si)-**III**; lower curve) and the protonated form (HCl vapour) [(4-pyH)(CH₂)₂-(Si)-]Cl (upper curve). Both were recorded in air.

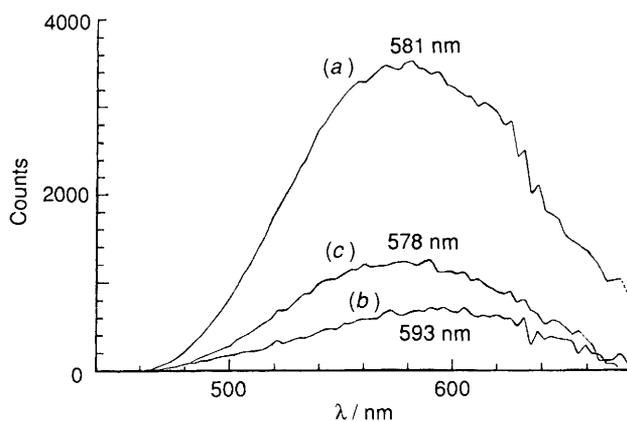


Fig. 3 Emission spectra of [fac-Cl(CO)₃Re(4-Me-bpy-4'-(CH₂)₄-(Si)-] **I** at the (a) cyclohexane-film, (b) acetonitrile-film and (c) air-film interfaces

coverage can be controlled. With regard to interpretation of the Γ_{bpy} and Γ_{Rebpy} values, if a disordered surface is assumed where a py or bpy 'headgroup' occupies an approximate rotational radius about the methylene chain of 4.5 and 12.5 Å respectively, values of 1.2×10^{-9} and 1.8×10^{-10} mol cm⁻² are obtained for monolayer coverage from closest packing arguments. These are similar to those reported in Table 1. Also shown in Table 1 are the results of contact angle measurements using the sessile drop method (water) for plates of known surface coverage. For comparison several other surfaces are also shown. The ordering of hydrophobicity is seen to be Ph > bpy ≈ Rebpy > Br ≈ py (full coverage) > pyH⁺.

Preliminary reactivity studies of both py and bpy surfaces have been conducted. Fig. 2 compares the UV spectrum of **III** before and after exposure to HCl gas. Protonation occurs as evidenced by both the appearance of the new transition at 221 nm and the increase in intensity and slight shift to higher energy of the 255 nm transition. The protonated form can then be reacted with either aqueous NaHCO₃ Et₃N in MeCN to regenerate the pyridine surface. Reaction of **II** with Re(CO)₅Cl in hot diglyme produces **I** which by UV-VIS spectroscopy has Γ_{Rebpy} values in the range of 2×10^{-10} mol cm⁻², i.e., close to that of the original Γ_{bpy} value of the uncomplexed surface (using $\epsilon_{s,370} = 3.7 \times 10^6$ cm² mol⁻¹). Of particular interest for future studies on energy and electron transfer on surfaces is that metal-to-ligand charge transfer luminescence of the Rebpy chromophore⁸⁻¹⁰ is easily seen at

both the air–film and solvent–film interface. Fig. 3 shows the relative emission intensity and emission maximum (E_{em}) in cyclohexane, air and MeCN. Although these measurements are for air-saturated solutions, the emission intensity variation is most likely a measure of quantum yield variations inherent to the solvent–chromophore interaction since the oxygen solubility (and the expected O_2 quenching rates) in hydrocarbons and MeCN is comparable. The E_{em} values are more revealing in that the luminescence of **I** is displaced *ca.* 30 nm to higher energy than that of the model complex *fac*-Re(4,4'-dmbpy)(CO)₃Cl for MeCN. That is, it is displaced towards the cyclohexane value. This is consistent with a less polar solvation sphere surrounding the complex than that of the pure solvent.^{10–13} At the air–film interface E_{em} is nearly the same as for cyclohexane. Evidently, the Rebpy chromophore serves as a sensitive reporter group^{10–14} for the local medium effects within the film, indicating that the hydrocarbon 'tail' dominates the solvent effect. This strongly argues for little solvent penetration (at least for MeCN) between the Rebpy headgroups and the fused silica surface.

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