Coordination Chemistry at a Surface: Polymetallic Complexes prepared on Quartz by Alternate Deposition of Iron(II) and Ruthenium(II) Centres

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Polymetallic complexes having well defined geometries are prepared *via* attachment of an anchor ligand to a quartz surface followed by repeated sequential reaction with $[Fe(OH_2)_6]^{2+}$ and a Ru^{II} complex having two tridentate bridging ligands rigidly fixed at 180°, $[(tpy-ph-tpy)_2Ru]Cl_2$ [tpy-ph-tpy = 1,4-di(2,2',6',2''-terpyridin-4'-yl)benzene].

The development of chemical methods for preparing molecular thin films at surfaces has advanced recently to include reactions involving covalent bond formation, ionic interactions and hydrogen bonding.[1–4] However, only few examples exist in which coordination chemistry is employed in the growth of thin film modified surfaces.[5,6] Some work has been done to illustrate the formation of monolayers of transition metal complexes covalently attached to surfaces *via* reaction of a metal complex with an anchor ligand covalently attached to a surface to yield an inert complex.[7] This work illustrates the preparation of films containing up to 10 metal centres *via* repeated sequential reaction of a labile complex, $[Fe(OH_2)_6]^{2+}$, and a substitutionally inert complex having two available tridentate bridging ligands attached $[(tpy-ph-tpy)_2Ru^{II}]Cl_2$ [tpy-ph-tpy = 1,4-di(2,2',6',2''-terpyridin-4'-yl)benzene], with a surface modified with an anchor ligand. The substitutional chemistry and electronic spectroscopy of tpy-ph-tpy complexes has been described by Sauvage *et al.*[8] The method for surface derivatization is shown in Scheme 1; all the reactions were carried out under an N_2 blanket. Quartz substrates are prepared by immersion in 'piranha' solution (70:30 H_2SO_4: 30% H_2O_2) for 6 h followed by repeated rinsing with distilled water and drying at 80 °C for several hours. Surfaces are initially treated with 3-bromopropyltrichlorosilane following well established methods [Scheme 1(*a*)].[9] Quartz pieces are heated under reflux in a 5% solution of the trichlorosilane in dry THF for 1.5 h. The pieces are removed from the THF, rinsed extensively with THF and acetone and oven dried. The anchor ligand, 4'-(4-methylphenyl)-2,2',6',2''-terpyridine, is attached following the method reported by Sullivan and coworkers.[7] In the procedure, deprotonation of the methyl of the terpyridine is followed by nucleophilic substitution at the surface bound bromomethyl group [Scheme 1(*b*)] upon immersing the slide in the THF solution for 3 h. The quartz slides are sonicated in $CHCl_3$ for a minimum of 20 min following each of the above reactions. Steps (*c*) and (*d*) are then repeated to prepare films at the quartz surface. Treatment of the surface with aqueous ethanolic solutions (1:1 v/v) of iron(II) ammonium sulfate (5 × 10⁻⁴ mol dm⁻³) for 3 h results in films having Fe^{II} coordinated to the terpyridine ligands. Subsequent reaction with $[(tpy-ph-tpy)_2-Ru^{II}]Cl_2$ dissolved in water–ethanol mixtures (1:1 v/v) under reflux for 3 h led to formation of films containing both metals. The quartz slides are again sonicated for 20 min in both water and ethanol, dried in an oven at 50 °C, and examined by contact angle and spectrophotometric methods after each cycle of steps (*c*) and (*d*). The sonication–drying procedure is repeated until absorption spectra have long wavelength absorbance matching the uncoated slide. No film growth is observed if immersion of

the slides in the Fe^{II} solution is omitted. Material adsorbed to the surface is removed during sonication of the supports.

Spectrophotometric changes observed after deposition of each cycle of steps (*c*) and (*d*) are shown in Fig. 1. The
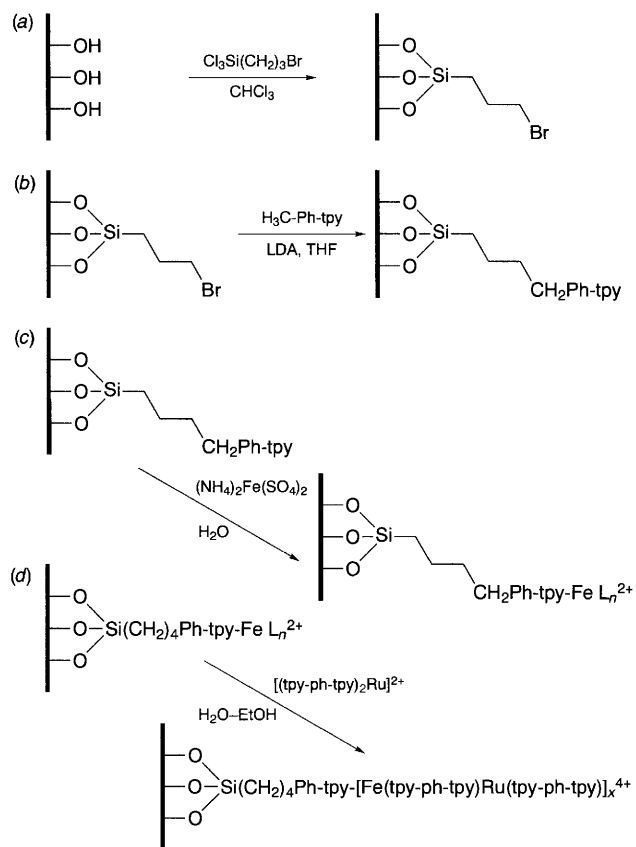
Scheme 1 Si linkage to surface idealized; $x = 1,2,3,...; x = 1$ for first cycle and increases with repeat of steps (*c*) and (*d*)
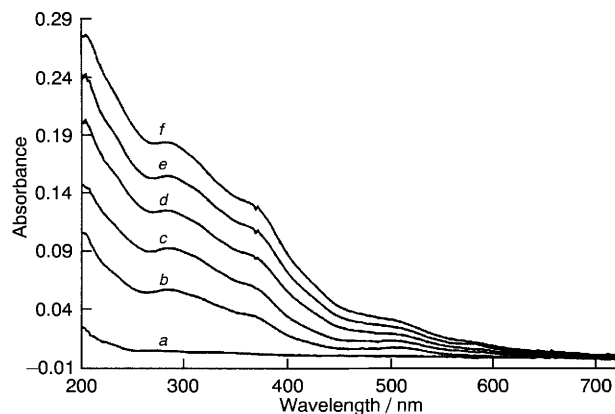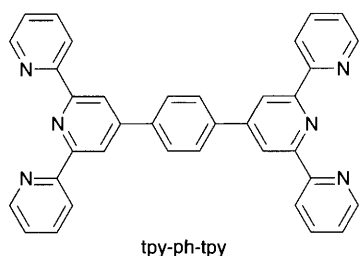

tpy-ph-tpy

Fig. 1 UV–VIS spectra of films following successive layer formation. (*a*) = $-Si(CH_2)_3Ph-tpy$; (*b*) = $-Si(CH_2)_3Ph-[tpyFe(tpy-ph-tpy)Ru(tpy-ph-tpy)]_n^{4n+}$ ($n = 1$); (*c*)–(*f*), $n = 2$–5.

absorption spectrum of the resulting film resembles that obtained from a solution containing a 1:1 mixture of $[Fe^{II}(mptpy)_2]^{2+}$ and $[Ru^{II}(mptpy)_2]^{2+}$ [mptpy = 4'-(4-methylphenyl)-2,2',6',2''-terpyridine]. All the transitions of the surface bound complex are broadened relative to the solution spectrum, but all the expected bands are present. The shoulder at 590 nm arises from the $Fe^{II} \rightarrow$ mptpy MLCT transition and the maximum at approximately 505 nm is the $Ru^{II} \rightarrow$ mptpy MLCT transition. The more intense absorptions at shorter wavelengths correspond to a mixture of MLCT and ligand localized transitions.

Contact angle measurements of the surface prior to derivatization illustrated that the surface was very hydrophilic since the advancing contact angle prior to derivatization of the surface was 22°. After deposition of the silane the angle increased to 65°. The angle after each cycle of Fe^{2+} and the Ru complex was between 62 and 66° when the counterion for the complex was perchlorate. Smaller angles were observed for surfaces when Cl^- served as the counterion.

From the absorption spectra of Fig. 1 it is determined that the largest absorbance increase occurs in the first cycle, after which the absorbance change per layer deposited increases linearly. A variety of explanations could account for the greater absorbance in the first cycle. Surface roughness could result in some regions where step (d) leads to reaction of Fe with both available bridging terpyridine ligands on the Ru centre. The flexibility of the butyl chain linking the silicon surface attachment site and the terpyridine ligand could also result in the formation of closed structures following step (d) [i.e. Si–(tpy)Fe(tpy-tpy)Ru(tpy-tpy)Fe(tpy)–Si].

The coverage of the surface can be estimated from the absorbance change observed per deposition cycle by making use of the solution molar absorptivity as a measure of the two-dimensional absorption coefficient. The molar absorptivity of a 1:1 mixture of the Fe^{II} and Ru^{II} complexes at 500 nm is 3.0×10^7 cm^2 mol^{-1}. The absorbance change in deposition cycles beyond the first cycle is approximately 0.003 per layer, yielding a coverage of approximately 1×10^{-10} mol cm^{-2}. This coverage indicates the surface area occupied per molecule to be ca. 166 Å^2. If each [tpyFe(tpy-tpy)Ru(tpy-tpy)] segment is

viewed as a cylinder having a radius of 5.7 Å (the distance from the metal centre to the periphery of the tpy), the maximum coverage for the cylinders aligned perpendicular to the surface is 1.6×10^{-10} mol cm^{-2} and the area per molecule is estimated to be 102 Å^2. The implication is that, neglecting surface roughness, the coverage achieved in this surface modification procedure is slightly more than half a monolayer. This is similar to coverages obtained in covalently linked monolayers of other metal complexes.[7]

References

1 See A. Ulman, *An Introduction to Ultrathin Organic Films: From Langmuir–Blodgett to Self-Asembly*, Harcourt Brace Jovanovich, Boston, 1991.
2 R. Maoz, L. Netzer, J. Gun and J. Sagiv, *J. Chim. Phys.*, 1988, **85**, 1059; A. Tillman, A. Ulman and T. L. Penner, *Langmuir*, 1989, **5**, 101.
3 S. D. Evans, A. Ulman, K. Goppert-Berarducci and L. Gerenser, *J. Am. Chem. Soc.*, 1991, **113**, 5866; Y. Lvov, F. Essler and G. Decher, *J. Phys. Chem.*, 1993, **97**, 13773; J. Schmitt, T. Grünewald, K. Kjaer, P. Pershan, G. Decher and M. Lösche, *Macromolecules*, 1993, **26**, 7058; D. Ingersoll, P. Kulesza and L. Faulkner, *J. Electrochem. Soc.*, 1994, **141**, 140.
4 L. Sun, L. Kepley and R. Crooks, *Langmuir*, 1982, **8**, 2101.
5 D. Li, D. C. Smith, B. Swanson, J. Farr, M. Paffet and M. Hawley, *Chem. Mater.*, 1992, **4**, 1047.
6 C. Bell, M. Arendt, L. Gomez, R. Schmehl and T. Mallouk, *J. Am. Chem. Soc.*, 1994, **116**, 8374.
7 S. Paulson, K. Morris and B., Sullivan, *J. Chem. Soc., Chem. Commun.*, 1992, 1615.
8 J. P. Sauvage, J. P. Collin, J. C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. DeCola and L. Flamigni, *Chem. Rev.*, 1994, **94**, 993.
9 R. Anderson, G. L. Larson and D. C. Smith, in *Silicon Compounds: Register and Review*, Hüls America Inc., Piccataway, NJ, 5th edn., p. 64.