Covalent surface confinement of osmium–terpyridine complexes: a UV–VIS and XPS study

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Well defined monolayers of $–Si(CH_2)_4Ph–tpy–OsCl_3$, $–Si(CH_2)_4Ph–tpy–Os(tpy)$ and $–Si(CH_2)_4Ph–tpyOsCl–(PPh_2)_2C{=}C{=}C(PPh_2)_2–Os(bpy)_2$ (tpy = 2,2′:6′,2″-terpyridine, bpy = 2,2′-bipyridine) on polycrystalline quartz surfaces are prepared and studied by UV–VIS and X-ray photoelectron spectroscopy.

Well defined monolayers and multilayers containing chromophores and redox-active centers are important owing to their diverse applications in photocatalysis, light-harvesting, nonlinear optical materials, and sensor technology.[1–5] We report here the preparation of monolayers and multilayers containing covalently confined osmium–terpyridine chromophores and the subsequent characterization using electronic absorption and X-ray photoelectron spectroscopy. Osmium–terpyridine complexes are known to be photostable and have well known solution-state absorption, luminescence, and redox properties.[6] Upon incorporation into the self-assembled organosilane monolayer structures *via* covalent linkage, surface-confined osmium–terpyridine units, in combination with other building block modifications, may allow the expedient assembly of robust monolayer and multilayer structures.

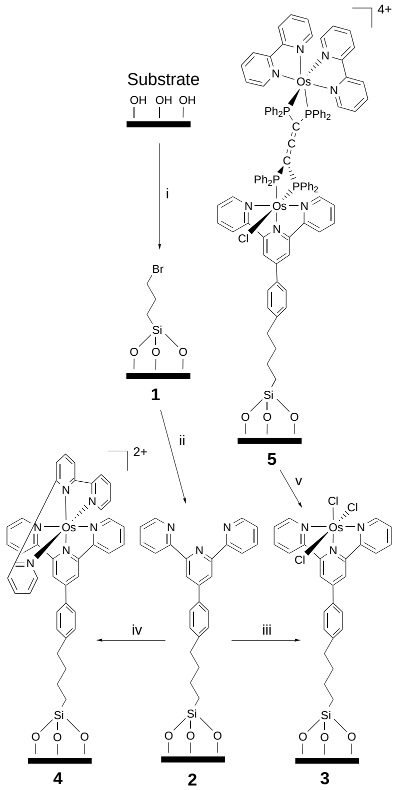
Scheme 1 illustrates the present approach to Os-containing monolayers and multilayers on polycrystalline quartz surfaces. It involves the initial direct reaction of a carbanion derived from a methyl-substituted terpyridine ligand with a preformed bromoalkylsilane surface,[4,5] giving a hydrocarbon tether to the quartz surface (Scheme 1, steps i and ii). The subsequent attachment of $OsCl_3$ to the modified surface was obtained by refluxing in aqueous ethanolic solution of $OsCl_3{\cdot}3H_2O$ for 3 h. The surface treatment with $Os(tpy)Cl_3$ (tpy = 2,2′:6′,2″-terpyridine), in the presence of NH_4PF_6, step iv, was carried out in a similar way but with much longer refluxing time (up to 3 d) to ensure the completion of surface attachment. This results in the monolayer **4** with terminal –tpy–Os–tpy units.

Also shown in Scheme 1, the terminal $OsCl_3$ units in monolayer **3** can be used as structural motifs in the further construction of multilayer structures, since Cl ligands can be replaced by σ or π ligands such as phosphine or polypyridine units in other molecular building blocks. Step v shows a representative reaction of surface confined $–OsCl_3$ units with a monometallic building block $[Os(bpy)_2\{(PPh_2)_2C{=}C{=}C(PPh_2)_2\}[PF_6]_2$† (bpy = 2,2′-bipyridine) in refluxing thf for 24 h,[7] giving the bilayer thin film **5**.

Spectrophotometric changes are monitored during the surface treatment using UV–VIS spectroscopy. Polycrystalline quartz has no significant absorption above 250 nm. Upon surface modification, typically we observe a weak increase of absorption after attachment of $–Si(CH_2)_4Ph–tpy$. Broad absorption bands at about 280 and 320 nm are observed upon addition of Os centers. The intensity of these two peaks increases as a function of reaction time and reaches maximum after three days. No significant increase or decrease in absorbance is observed after 3 d, indicating that a stable monolayer with terminal $–CH_2Ph–tpy–Os–tpy$ units is obtained.

The UV–VIS spectrum of the solution sample of $Os(ttp)(tpy)(PF_6)_2$‡ (ttp = $CH_3Ph–tpy$) has absorption bands at 275 nm (ε = 28 430 $dm^3\ mol^{-1}\ cm^{-1}$), 315 (43 100), 485 (11 490) and 665 (2840). When compared with the solution sample, the observed transition bands of the surface bound $–CH_2Ph–tpy–Os–tpy$ units in sample **4** are relatively broad and slightly shifted (shift *ca*. 5 nm towards longer wavelength), and tailed into 500 nm. However, no significant ^{3}MLCT band in the range 500–700 nm is observed for the surface samples with attached Os centers owing to the much lower absorption coefficient of the band at 665 nm.§

The calculation of surface coverage, using UV–VIS spectroscopy, has also been carried out. The solution ε_{max} values were assumed to be invariant in order to provide an approximation to the two-dimensional surface absorption coefficients (ε_s) in the calculations.[4,5] Using the lowest energy π–π* transition at 280 nm, the estimated values of monolayer surface coverages for modified surfaces with terminal $–CH_2Ph–tpy–Os–tpy$ ($\varepsilon_{s,280} = 2.8 \times 10^7\ cm^2\ mol^{-1}$) and $–CH_2Ph–tpy–OsCl_3$ ($\varepsilon_{s,280} = 1.2 \times 10^7\ cm^2\ mol^{-1}$) units are 2.0×10^{-10} and 3.6×10^{-10} mol cm^{-2}, respectively. These values are comparable with the reported values (typically, 1×10^{-10} mol cm^{-2}) of the surface coverages for monolayers with complexes of Fe, Ru or Re.[4,5] The estimated surface coverage for bilayer with $–CH_2Ph–tpy–$



Scheme 1 *Reagents and conditions*: i, $Br(CH_2)_3SiCl_3$, thf, ambient temp.; ii, 4′-tolyl-2,2′ : 6′,2″-terpyridine and LDA, thf, ambient temp.; iii, $OsCl_3{\cdot}3H_2O$, EtOH–H_2O (1 : 1), reflux 3 h; iv, $[Os(tpy)Cl_3]$, NH_4PF_6, EtOH–H_2O (1 : 1), reflux for up to 3 d; v, $[Os(bpy)_2\{(PPh_2)_2C{=}C{=}C(PPh_2)_2\}][PF_6]_2$, thf, reflux 24 h

Table 1 X-Ray photoelectron spectroscopic analysis of modified surfaces

	Binding energy/eV							
Surface-confined units[a]	Si 2p	O 1s	C 1s	Br 3d	N 1s	Os 4f	Cl 2p	P 2p
$-Si(CH_2)_3-Br$ **1**	107.15	536.40	288.40	74.60				
$-Si(CH_2)_3-ttp$ **2**	106.20	535.80	287.85		402.40			
$-Si(CH_2)_3-ttp-OsCl_3$ **3**	106.20	535.80	287.85		402.40	53.85 56.45	200.00	
$-Si(CH_2)_3-ttp-Os-tpy$ **4**	105.80	535.95	287.60		402.75	53.80 56.40		
$-Si(CH_2)_3-ttp-OsCl-P_4C_3-Os(bpy)_2$ **5**	106.00	535.50	287.85		402.40	53.30 55.90	—[b]	—[b]

[a] P_4C_3 = $(PPh_2)_2C{=}C{=}C(PPh_2)_2$; ttp represents a $-CH_2Ph-$tpy unit. [b] Not observed; P peak position overlaps with Si.

$OsCl[(PPh_2)_2C{=}C{=}C(PPh_2)_2]Os(bpy)_2$ ($\varepsilon_{s,280}$ = 4.4×10^7 cm^2 mol^{-1}) units is 2.7×10^{-11} mol cm^{-2}.

We have monitored each surface modification step by studying the modified surfaces by XPS (Fig. 1).[8] The elements involved in our modification procedures have their characteristic binding energies which can be clearly identified. Representative XPS data observed in each modification step are included in Table 1. Specifically, the successful modification of quartz surfaces by 3-bromopropyltrichlorosilane (step i) was verified by observation of Br 3d XPS (74.60 eV) in addition to Si 2p (107.15 eV), O 1s (536.40 eV) and C 1s (288.40 eV). Upon further reaction of terminal Br group with lithiated ttp ligand, step ii, N 1s (402.40 eV) is observed, while no significant Br 3d peak is found. After step iii or iv, XPS analysis gives Os 4f at 53.85 eV ($4f_{7/2}$) and 56.45 eV ($4f_{5/2}$) for sample **3** as well as 53.80 eV ($4f_{7/2}$) and 56.40 eV ($4f_{5/2}$) for sample **4**, all of which are characteristic of the Os 4f peaks.[9] Upon further addition of the $Os(bpy)_2[(PPh_2)_2C{=}C{=}C(PPh_2)_2]$ unit, the observed Os 4f peaks in sample **5** shifted to slightly lower energies, with 53.30 and 55.90 eV for $4f_{7/2}$ and $4f_{5/2}$, respectively. Since there are both Os^{III} and Os^{II} centers in **5** and the reported energies of 4f peaks of Os^{II} are slightly lower than those of Os^{III} {*i.e.*, with the same types of ligands, $4f_{7/2}$ is *ca.* 50.2–50.8 eV in $[Os^{II}Cl_2(PhPMe_2)_4]$ and *ca.* 51.4–52.0 eV in $[Os^{III}Cl_3(PhPMe_2)_3]$[9]}, the small shift of Os 4f peaks in **5** towards the lower energy region may be, partly, due to the overlapping Os 4f peaks of both Os^{II} and Os^{III} centers. No XPS peak corresponding to P can be unambiguously identified owing to the overlap of its peak with that of Si. Efforts have also been made to identify the peak corresponding to the inner Cl ligand on the Os^{III} center in **5**, but no significant peak is observed.

A control experiment has been carried out in order to verify whether Os-based units could, instead of a covalent linkage, adsorb on quartz surfaces. After we refluxed $OsCl_3$ or $[Os(tpy)(ttp)(PF_6)_2]$ with clean quartz slides (no modification steps i–ii used) in $EtOH-H_2O$ for 3 d and followed the same cleaning procedures, no significant change was observed in either UV–VIS or XPS analysis of treated surfaces when compared with that of clean quartz surface. This indicates that without the modification steps i and ii, Os-based units cannot be attached to quartz surfaces.

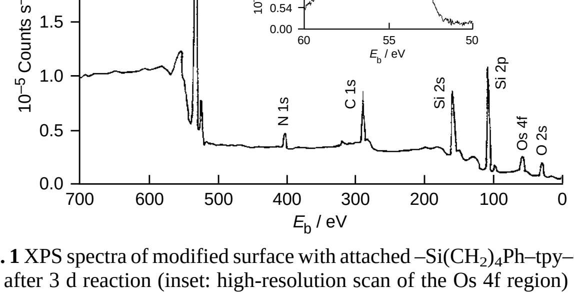


Fig. 1 XPS spectra of modified surface with attached $-Si(CH_2)_4Ph-$tpy–Os–tpy after 3 d reaction (inset: high-resolution scan of the Os 4f region)

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Footnotes and References

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† Preparation of $Os(bpy)_2[(PPh_2)_2C{=}C{=}C(PPh_2)](PF_6)_2$. $(PPh)_2C{=}C{=}C(PPh_2)$[10] (296 mg, 0.38 mmol) in 15 ml thf was heated to reflux under N_2, and $[Os(bpy)_2Cl_2]\cdot 2H_2O$ (100 mg, 0.16 mmol) in ethylene glycol was added dropwise. The resulting solution was refluxed for 2 h, and excess NH_4PF_6 was added. The solution mixture was then refluxed for 60 h. Upon removal of thf, the solution was added dropwise to 100 ml of saturated aqueous KPF_6 solution. The precipitate thus formed was collected by vacuum filtration. Yield: 89%. $^{31}P\{^1H\}$ NMR (CD_3CN, 202 MHz, 22 °C): δ −30.49, −37.37. FABMS: *m/z* 1425 ($M - PF_6$)$^+$.

‡ *Preparation of* $[Os(tpy)(ttp)(PF_6)_2]$: $[Os(tpy)(H_2O)_3][PF_6]_3$ (50 mg, 0.09 mmol) and ttp (50 mg, 0.15 mmol) were heated at *ca.* 150 °C in ethylene glycol for 1 h. The resulting solution was added dropwise to 100 ml of saturated aqueous KPF_6 solution to induce precipitation. The brown product was collected *via* vacuum filtration and washed with distilled water (3×20 ml). FABMS: *m/z* 893 ($M - PF_6$)$^+$. ^1H NMR (CD_3CN): δ 2.56 (s, 3 H, CH_3), 7.06–9.01 (25 H, m, Ar-H).

§ For surface-confined Os(tpy)(ttp) units, ε at 665 nm is only *ca.* 6–10% of the values at 275 or 315 nm. Hence, the expected absorbance would be a much lower value (*ca.* 0.0005–0.001) at 665 nm.

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