Adsorption of ruthenadendrimers to silica–titania surfaces studied by optical waveguide lightmode spectroscopy (OWLS)

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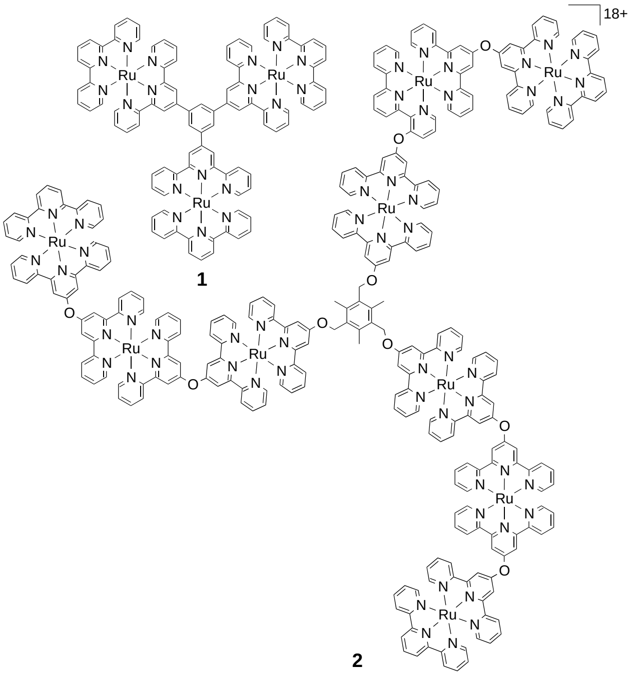
Kinetic analysis of the assembly of metallodendrimers at silica–titania surfaces shows that the deposition mode strongly depends on the bulk concentration.

Metallodendrimers are potentially key components for future generations of ultraminiature computing, sensing and photoconversion devices. We are developing a methodology for the incorporation of metallodendrimers into nanostructured composites that relies on the assembly of mono- or multi-layers on substrate surfaces in contact with solutions of the desired component. Here we describe the use of optical waveguide lightmode spectroscopy (OWLS) for studying the assembly of surface layers of metallodendrimers on smooth silica–titania.

Our initial studies were made on the rigid triruthenium complex **1**[1] and the more flexible nonaruthenium compound **2**.[2] The measurements are based on the observation that the modes of an unclad waveguide shift their energies in response to changes in the waveguide environment.[3,4] Planar optical waveguides are particularly convenient for probing surface deposition processes[4,5] not only because of their well defined geometry, but also because they can be fabricated from a wide variety of different materials. The mode spectrum can be very conveniently and accurately measured using a grating coupler.[6] In order to maximize the sensitivity of the measurements,[6] we used thin waveguides supporting only the zeroth order transverse magnetic (TM) and transverse electric (TE) modes. Measurement of the mode energies, expressed as effective refractive indices N, enabled the two optogeometric parameters characterizing the deposited layer, thickness d_A and refractive index n_A, to be determined.[4,6] From these the surface density (Gibbs excess) Γ in molecules per unit area can be calculated from:[4]



1

2

$$\Gamma = d_A(n_A - n_C)/(dn/dc) \quad (1)$$

where n_C is the refractive index of the covering medium (in our case, acetonitrile), and dn/dc is the refractive index increment of the compound, determined using a Rayleigh interferometer (1.45 and 0.49 dm^3 mol^{-1} for **1** and **2**, respectively). As substrates for adsorption, we used Si(Ti)O$_2$ planar optical waveguides. They were fabricated by oxidatively sputtering a Si/Ti target onto an optical glass support into which a shallow (*ca*. 10 nm) grating coupler (grating constant $\Lambda = 833.\dot{3}$ nm) had been photolithographically etched. Their surface composition was $Si_{0.76}Ti_{0.24}O_2$, measured using X-ray photoelectron spectroscopy, and their mean roughness was 0.12 ± 0.05 nm, measured using atomic force microscopy. A cylindrical cuvette (diameter = 9 mm) was sealed to the grating region of the waveguide using a 'Kalrez' O-ring and the mode spectrum measured at 632.8 nm. The baseline spectrum was recorded with pure acetronitrile (Baker spectroscopic grade) flowing through the cuvette. Flow was then switched to a solution (concentration c_b) of **1** or **2** in acetonitrile, while continuing to measure the mode spectrum. After an adsorption plateau appeared to have been attained, flow was switched back to pure acetonitrile. Desorption was negligible, except for the deposition of **2** at the largest bulk concentration tested (0.2 mM).

Transport to the surface is *via* convective diffusion and hence governed by a law of the type:

$$d\Gamma/dt = Dc_b/\delta \quad (2)$$

where δ is the thickness of the diffusion boundary layer[7] (*ca*. 80 µm in our experiments[8]), and D the diffusivity of the molecules in acetonitrile (estimated from the dimensions of the molecule as 8×10^{-6} cm^2 s^{-1}).

Fig. 1 shows representative measurements of Γ *vs*. t. The initial deposition rates dΓ/dt are much lower than predicted by eqn. (2), implying that energy barrier and/or orientational

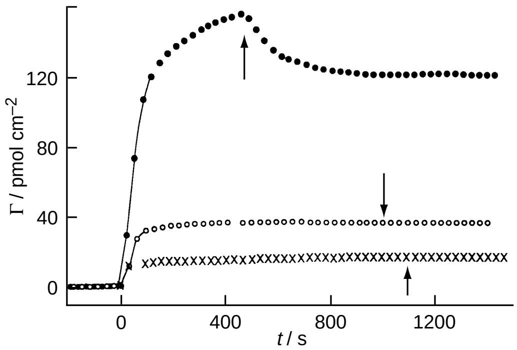


Fig. 1 Representative experimental data: (×) **1**, c_b = 4 µM; (○) **2**, c_b = 2 µM; (●) **2**, c_b = 200 µM. Bulk flow was switched to the ruthenadendrimer solution at t = 0. The arrows denote when the flow reverted to pure buffer.

factors result in not every adsorption attempt being successful. Furthermore, the rate of deposition decreases with time, but since there is no desorption, this cannot be due to the establishment of an equilibrium, but rather to the progressive blockage of the adsorbing surface as molecules adsorb. Hence eqn. (2) must be modified to take these effects into account.

We do this by considering a layer of solution just above the plane of adsorption. Let the concentration of metallodendrimers in this plane be c_1. The rate of deposition is, per unit area S of surface, $Sk_ac_1\phi$. The chemical rate constant k_a is to a first approximation proportional to the product $\kappa\exp(-E_a)$, where κ is the probability that the incoming molecule arrives in an orientation permitting incorporation into the surface adlayer, and E_a is the energy barrier (electrostatic, *etc.*) hindering adsorption. ϕ is the fraction of the surface available for adsorption. Since the molecules are deposited at random onto a continuum, the dependence of ϕ on θ, the fraction of the surface occupied ($\theta = \Gamma a$, a being the area occupied per molecule) is not straightforward.[9,10] Analysis of the geometry of deposition, using the concept of exclusion zones, leads to the expression:[9]

$$\phi = \frac{(1-\tilde{\theta})^3}{1-0.812\tilde{\theta}+0.2336\tilde{\theta}^2+0.0845\tilde{\theta}^3}. \tag{3}$$

Here $\tilde{\theta} = \theta/\theta_J$; θ_J (*ca.* 0.55 for disk-shaped objects[9]) is the jamming coverage, at which no spaces large enough to accept a further molecule exist on the surface.

Diffusion from the bulk to the layer above the surface follows the usual Fick–Smoluchowski kinetics, and hence

$$(V/S)(\mathrm{d}c_1/\mathrm{d}t) = (c_b - c_1)D/\delta - k_ac_1\phi \tag{4}$$

where V is unit volume. By letting the left hand side go to zero, an expression for c_1 is obtained, which is used to obtain a corrected rate law:

$$\mathrm{d}\Gamma/\mathrm{d}t = c_b/[\delta/D + 1/(k_a\phi)] \tag{5}$$

This equation was fitted to the experimental data transformed by numerical differentiation into dΓ/dt *vs.* Γ plots, with a and k_a as free parameters. The results are given in Table 1. Also shown in the extreme right hand column is the product of the apparent plateau value of Γ read off the experimental curves and the fitted a: the agreement with the expected jamming coverage θ_J of 0.55 is satisfactory. This is itself a strong indication that the random sequential adsorption (RSA) model[9,10] applies; further evidence is that eqn. (5), with ϕ given by eqn. (3), fitted all the transformed curves (except for compound **2** at c_b = 20 nM, for which the Γ *vs.* t plot consisted of two linear portions). There was no evidence for surface diffusion of the adsorbed molecules (which leads to dΓ/dt decreasing linearly with Γ).[11]

Table 1 Parameters derived from fitting eqn. (5) to the experimental data

	c_b/μM	a/nm^2	k_a/cm s^{-1}	Γ_∞[a]/ pmol cm^{-2}	$a\Gamma_\infty$[b]
1	0.4	5.7	2.1×10^{-3}	16	0.61
	4	6.0	2.0×10^{-3}	17	0.56
	40	5.7	2.0×10^{-3}	17	0.58
2	0.02	—[c]	1.6×10^{-4} [c]	35	—[c]
	0.2	2.3	1.4×10^{-1} [d]	42	0.58
	2	2.4	7.0×10^{-3}	40	0.58
	20	1.8	2.0×10^{-4}	55	0.59
	200	0.51	4.3×10^{-5}	42	0.51

[a] The value of Γ at saturation, estimated from the experimental curves. [b] *i.e.* θ_J (*cf.* the theoretial value of 0.55 for spheres/disks[9]). [c] Could not be determined since eqn. (5) did not fit the data. $\Gamma(t)$ consisted of two linear portions, with slope 3.2 fmol cm^{-2} s^{-1} initially, up to Γ = 27 pmol cm^{-2}, *i.e.* $\theta \approx 0.4$, assuming $a \approx 2.4$ nm^2, and 0.3 fmol cm^{-2} s^{-1} thereafter, with no indication of exclusion effects. The given value of k_a was obtained by dividing the initial rate by c_b. [d] Preceded by a linear portion up to Γ = 34 pmol cm^{-2} yielding $k_a = 4.6 \times 10^{-4}$ cm s^{-1}.

Compound **1** followed pure random sequential adsorption kinetics. The parameters were almost invariant with c_b and consistent with the molecule lying flat on the surface.

Compound **2** behaved in a more complicated way, which differed qualitatively over the concentration range investigated. Since the molecule can adsorb to the surface in various conformations, the parameter a must be interpreted as an average area. Surprisingly, even though **2** is much bigger than **1**, the area it occupies is much smaller. We interpret this as the molecule attaching itself to the surface with only one of its arms. At the highest bulk concentration (0.2 mM), the adsorption shows a qualitatively different pattern: the amounts adsorbed are much higher, and unlike the layers assembled from lower c_b, they desorb to a significant degree. This appears to indicate the formation of a second layer only weakly attached to the first and hence removable upon dilution of the cover solution, an inference supported by the mean thicknesses d_A *ca.* 0.5 nm for $c_b \leqslant 20$ μM and 2.2 nm for $c_b \geqslant 0.2$ mM ('mean thickness' refers to the mean distance of the optically densest portion of the molecule from the adsorbing surface). The very small fitted a for c_b = 0.2 mM partly reflects the formation of the second layer, but it is in fact much less than half the value given by the lower c_b, and hence indicates that the molecules pack into a much more compact conformation within the layer. We propose that this is achieved *via* lateral interpenetration of the dendrimers: the RSA theory as developed hitherto[9,10,12] only considers smooth geometrical objects such as spheres, ellipsoids, *etc.*

These results demonstrate the primordial importance of bulk concentration in directing the self-assembly of complex molecules at surfaces.

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Footnote and References

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1 E. C. Constable and A. M. W. Cargill Thompson, *J. Chem. Soc., Chem. Commun.*, 1992, 617; *J. Chem. Soc., Dalton Trans.*, 1992, 3467; *J. Chem. Soc., Dalton Trans.*, 1995, 1615.
2 E. C. Constable, A. M. W. Cargill Thompson, P. Harverson, L. Macko and M. Zehnder, *Chem. Eur. J.*, 1995, **1** 360; E. C. Constable and P. Harverson, *Chem. Commun.*, 1996, 33; *Inorg. Chim. Acta*, 1996, **252**, 9.
3 P. K. Tien, *Rev. Mod. Phys.*, 1977, **49**, 361.
4 J. J. Ramsden, *J. Statist. Phys.*, 1993, **73**, 853.
5 J. J. Ramsden, D. J. Roush, D. S. Gill, R. G. Kurrat and R. C. Willson, *J. Am. Chem. Soc.*, 1995, **117**, 8511.
6 K. Tiefenthaler and W. Lukosz, *J. Opt. Soc. Am. B*, 1989, **6**, 209.
7 V. G. Levich, *Physicochemical Hydrodynamics*, Prentice Hall, Englewood Cliffs, NJ, 1962.
8 R. Kurrat, J. J. Ramsden and J. E. Prenosil, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 587.
9 P. Schaaf and J. Talbot, *J. Chem. Phys.*, 1989, **91**, 4401.
10 G. Tarjus, P. Schaaf and J. Talbot, *J. Chem. Phys.*, 1990, **93**, 8352.
11 J. J. Ramsden, G. I. Bachmanova and A. I. Archakov, *Phys. Rev. E*, 1994, **50**, 5072.
12 P. Viot, G. Tarjus, S. M. Ricci and J. Talbot, *J. Chem. Phys.*, 1992, **97**, 5212.

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