Molecular Recognition in a Monolayer Matrix on Silica Gel

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The molecular recognition on a template-modified monolayer matrix on silica was studied, with selectivity factors ranging from 1.7 to 5.6, depending on the structural differences in the competing pair.

Molecular recognition by polymers prepared by imprinting with templates has been studied intensively in recent years.[1,2] The selectivity observed in these systems is generally the result of the combination of cavity-shape fitting and the exact positional arrangement of the functional groups. However, there are disadvantages in using polymers as matrices. For example, the swelling of the polymer by organic solvents makes a site too flexible to be 'specific.' Diffusion rate differences of molecules into the polymer also complicate the origin of observed selectivity. Monolayer assemblies of long chain molecules[3] appear to be ideal systems in that the close-packing of molecular chains results in a more rigid system so that the exact placement of functional groups in such a system is more likely to be maintained. Also chemical processes occurring within a monolayer are less likely to be affected by diffusional differences. Here, we report the preliminary result of our investigations of molecule recog-

nition in a monolayer matrix containing specific binding sites prepared by the imprinting method on a silica gel surface.[†]

The template used for building the specific site was terephthal aldehyde (**1**). Compound (**1**) was attached to the silica gel surface through a diiminosilane linkage (**A**) at high dilution.[‡] The rest of the surface was covered by a monolayer

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[†] In ref. 1(b), hexamethyldisilazane was used to block the remaining silanol groups. However, this would not totally prevent binding of two molecules in one site or the binding of one molecule across two neighbouring sites.

[‡] Binding conditions: refluxing in toluene for 12 h, followed by azeotropic distillation of solvent. Acidic hydrolysis in acetonitrile afforded (**1**) as the only product in >95% yield, confirming the complete binding of the silane used. The amount used was expected to cover less than 15% of the surface area.
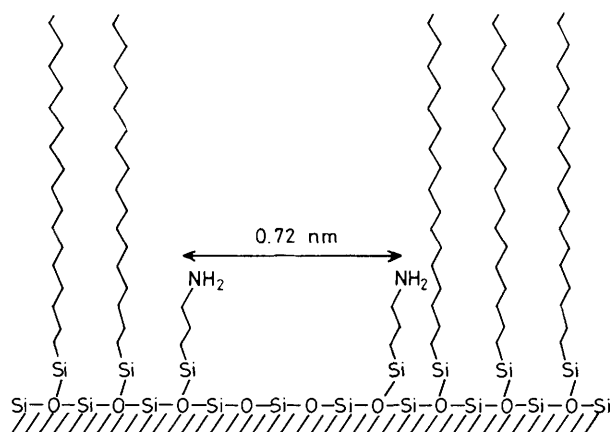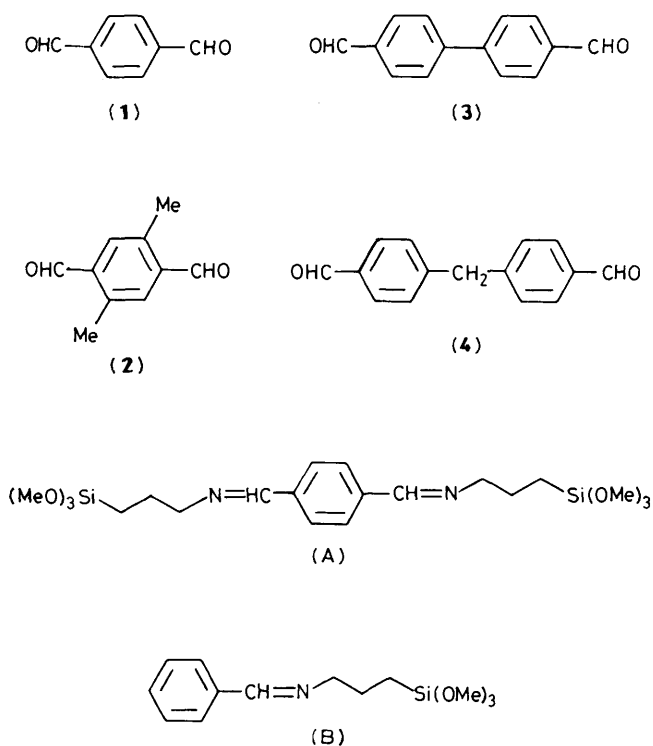
(1)

(3)

Me

(2)

(4)

(A)

(B)

Figure 1. Template (1)-modified monolayer matrix on silica.

Table 1. Selectivity of template-modified monolayer matrix on silica surface.

	Competing pair		
	(1)/(2)	(1)/(3)	(1)/(4)
Partition ratio on A-modified silica	1.67	2.10	2.32
Partition ratio on B-modified silica	0.95	1.02	0.41
Selectivity factor	1.75	2.06	5.65

of octadecylsilane.§ These long chain molecules served not only to isolate the template effectively,[4] but their tendency to pack closely afforded a rigid environment around the templates. Removal of (1) left behind an open space with a shape resembling that of compound (1) and with two amino groups, of $-NH_2 \cdots NH_2-$ separation ca. 0.72 nm (Figure 1). We investigated a series of competitive reactions between (1) and a range of different dialdehydes (2—4) with diamino-functionalized surface sites. As a control system, the mono-iminosilane (B) was used to create a surface with a random and non-specific amino group distribution. The results are shown in Table 1.

For the (1),(2) pair, both compounds have two aldehyde groups with inter-group separation similar to that expected between the amino groups at the binding site, yet they have different molecular shapes. If the template (1) was linked to the surface of silica gel with the molecular plane positioned

more or less perpendicularly, little or no selectively would be expected. The moderate selectivity observed indicates that the molecular plane is nearly parallel to the silica surface. Shape fitting therefore contributes to the observed selectivity. For the (1),(3) pair, the difference in the distance between the two aldehyde groups is only 0.4 nm [separation of aldehyde groups = 1.12 nm for (3)]. The selectivity is, however, only slightly higher than that for the (1),(2) pair. Compound (4), which has a non-linear shape and a distance of 1.05 nm between the aldehyde groups, reacts preferentially with the non-specific amino surface by a factor of 2.5 over (1). From a molecular model, it is not surprising that (4) is preferred for two-point attachment. Yet on the template-modified monolayer matrix, the situation is reversed. Thus the conformational preference for (4) is overridden owing to mismatching of the shape. The selectivity factor of 2.32 is slightly higher than that found for the (1),(3) pair, presumably mainly owing to 'shape-fitting' effects. Overall, a significant selectivity factor of 5.65 is calculated.

Thus imprinting within a monolayer matrix on the surface of silica provides a useful system to study the molecular recognition phenomenon. Application of this technique to differentiate between even smaller differences in compounds such as the presence of a linear or branched chain is being investigated in our laboratory.

§ The validity of monolayer coverage by octadecylsilyl chains alone was confirmed by elemental analysis. Furthermore, the amount of loading for C_{10}, C_{16}, and C_{18} silanes is similar, each corresponding to a molecular area of 22—25 Å.

References

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