Gable Porphyrin Metal Complex as a Double Recognition Model

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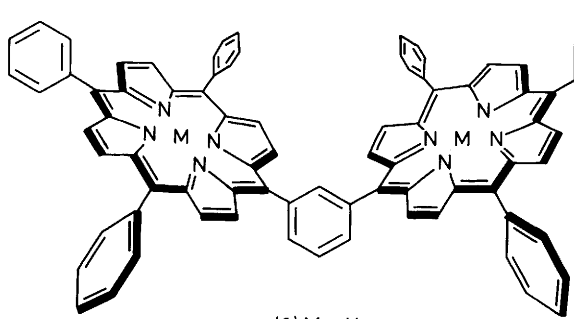
A new metalloreceptor, a gable porphyrin metal complex, recognizes aromatic heterocycles regiospecifically by the use of *double* recognition , which is necessary for advanced molecular recognition.

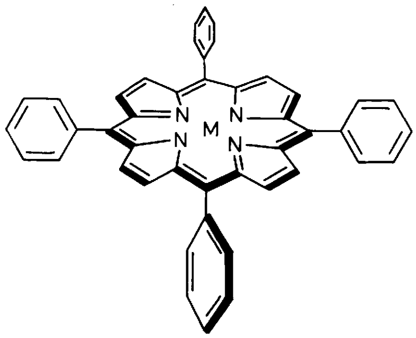
Molecular recognition, which plays an important role in biological systems, has been investigated intensively by bio-organic and organic chemists over the last 20 years.[1] For advanced molecular recognition, *multiple* recognition is essential. For *double* recognition, it has been reported that two subunits (two hydrophobic cavities,[2] two cationic sites,[3] or two carboxy groups in molecular clefts,[4] *etc.*) held at a certain distance, interacting with each other, have worked as artificial receptors. In spite of these studies, investigations of multiple recognition using metalloporphyrins as recognition sites have been made.[5] Metalloporphyrins fulfil many functions in biological systems, such as redox reactions, electron transfer, oxygen transport, and charge separation *etc.* An artificial receptor made of metalloporphyrins could open the way to designing an 'artificial catalytic receptor'.

This communication reports that the artificial receptor, which contains two porphyrin metal complexes in a fixed conformation, recognizes heterocycles (substrates) regiospecifically. The gable porphyrin metal complex (**1**) consists of two metalloporphyrin subunits linked by a *m*-substituted benzene spacer.[6a] The gable porphyrin zinc complex (**1a**) binds 4,4′-dipyridylmethane (**7**) very strongly ($K = 4.0 \times 10^6$ mol^{-1} dm^3) to form an artificial allosteric system.[6b] This strong affinity for aromatic heterocycles can also be used for substrate recognition of the metalloreceptor.

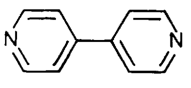
Binding constants were obtained by ligand titration using UV-visible spectra and calculated by a Hill plot. The estimated binding constants of substrates by the metalloreceptors dinuclear (**1a**) and mononuclear (**2a**) are listed in Table 1. It is known that zinc porphyrin forms a pentaco-ordinate



(1) M = H$_2$
(1a) M = Zn



(2) M = H$_2$
(2a) M = Zn



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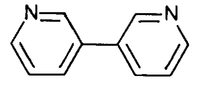

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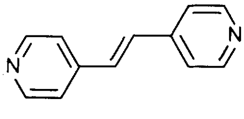

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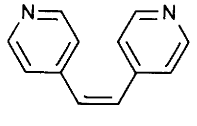

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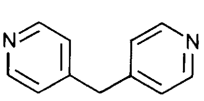

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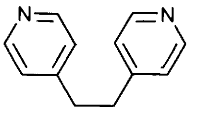

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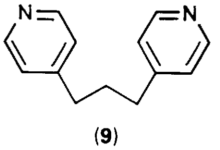
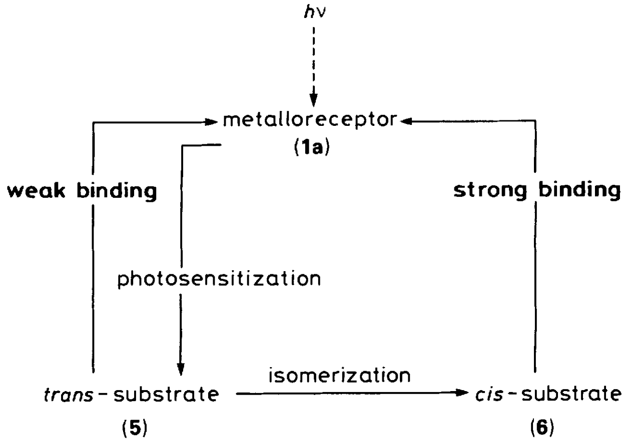


(9)

rather than a hexaco-ordinate adduct in organic solvent.[7] Even for a bifunctional substrate (**7**), the binding constant (K = 1.5×10^4 mol^{-1} dm^3 for the binary complex) of (**2a**) is not very different from that for a monofunctional ligand, picoline (K = 1.2×10^4 mol^{-1} dm^3). The bridged structure of the (**1a**) : (**7**) adduct has been confirmed by 1H NMR spectroscopy.[6b] Corey–Pauling–Koltun (CPK) modelling of the adduct shows that the complex is strained. The longer substrate (**8**) was bound to the gable zinc complex more strongly ($-\Delta G_{8-7}$ = 1.2 kcal mol^{-1}) (1 cal = 4.184 J). The basicity difference between (**7**) and (**8**) does not explain this selectivity [K for (**2a**) is 1.5×10^4 for (**7**), 2.0×10^4 mol^{-1} dm^3 for (**8**), respectively]. It may arise from the reduction of strain in the substrate–receptor complex. The longest substrate (**9**) is very strongly bound to (**1a**), with a binding constant exceeding 10^8 mol^{-1} dm^3. 3,3′-Dipyridyl (**4**) is bound to (**1a**) 9.5 times more strongly than 4,4′-dipyridyl (**3**). However, the ratio of the binding constants of (**3**) and (**4**) to the monomeric recepter (**2a**) was 1.2. This result indicates that metalloreceptor (**1a**) can recognize the shape of the substrates by double recognition. Metalloreceptor (**1a**) also binds *cis*-1,2-dipyridylethylene (**6**) moderately (K = 2.0×10^5 mol^{-1} dm^3). In contrast, the corresponding *trans*-isomer (**5**) showed no enhanced binding (K = 1.6×10^4 mol^{-1} dm^3); apparently a *cis* configuration is necessary for appropriate binding.



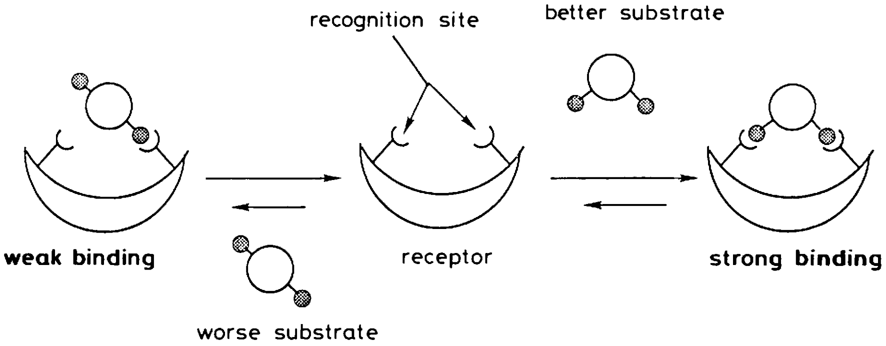
Scheme 1. Photosensitization and molecular recognition by metalloreceptor.

Table 1. Estimated binding constants of aromatic heterocycles to metalloreceptors (**1a**) and (**2a**).[a]

	Binding constant $K^b/10^3$ mol^{-1} dm^3		
	Dinuclear	Mononuclear	
Substrate	(**1a**)	(**2a**)	$K_{(1a)}/K_{(2a)}$
(**9**)	$>10^5$	23	>4300
(**8**)	3.2×10^4	20	1600
(**7**)[c]	4.0×10^3	15	270
(**6**)	2.0×10^2	8.9	22
(**5**)	1.6×10^1	17	0.94
(**4**)	1.6×10^2	11	15
(**3**)	1.7×10^1	13	1.3

[a] *Abbreviations*: (**1**) gable porphyrin free base; (**1a**) gable porphyrin dizinc complex; (**2**) tetraphenylporphyrin free base; (**2a**) tetraphenylporphyrin zinc complex; (**3**) 4,4′-dipyridyl; (**4**) 3,3′-dipyridyl; (**5**) *trans*-1,2-dipyridylethylene; (**6**) *cis*-1,2-dipyridylethylene; (**7**) 4,4′-dipyridylmethane; (**8**) 1,2-bis(4,4′-pyridyl)ethane; (**9**) 1,3-bis(4,4′-pyridyl) propane. [b] Benzene, 25 °C. [c] Ref. 6b.

At 1.0×10^{-6} M of (**5**) (L: ligand), [(**1a**) L]/[(**1a**)] was *ca.* 0.1. Under this condition, the dichloromethane solution was photoirradiated at 430 nm, which is a characteristic absorption maximum in the Soret band of (**1a**). After 20 min, the ratio of [(**1a**) L]/[(**1a**)] was increased to 0.99. At this concentration, (**5**) could not be photoisomerized within 20 min without the metalloreceptor. *trans* isomer (**5**) could also be photosensitized by the mononuclear receptor (**2a**) but could not be



Scheme 2. Schematic representation of molecular recognition using double recognition.

bound to it under these conditions. In order to bind substrate (**5**), the metalloreceptor is required to change the configuration of substrate (**5**) to that of (**6**) (Scheme 1).

Using this model system, three processes have been mimicked. Firstly, the substrate was bound to the metalloreceptor weakly. Then the substrate was forced to change to a configuration capable of interacting tightly. Finally, the metalloreceptor bound the substrate more strongly.

For specific recognition, complementarity in size, shape, and functional groups is very important.[1] Fixation of recognition sites with appropriate distances and directions is essential in order to use the complementarity principle. The distance between the metal centres in our model is 13 Å and the angle between the two porphyrin subunits of our metalloreceptor (**1a**) is 120°. Molecular recognition is realized by the summation of a number of these recognition sites, socalled multiple recognition. From this point of view, the metalloreceptor described resembles Rebek's model, comprising molecular clefts with convergent functional groups. Moreover, the metalloporphyrin has the advantage of being able to catalyse many redox reactions, so our metalloreceptor can also be modified as a reaction centre.

Using the metalloreceptor concept (see Scheme 2), we can design and synthesize host molecules with a multiple recognition site.[8] Further study of double[9] or multiple recognition using other metalloreceptors[10] is now underway.

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