Construction of a self-assembling porphyrin trimer system

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A quaternary self-assembling system consisted of three porphyrin molecules and one linker molecule is constructed.

The chemical construction of self-assembling systems is currently of interest to chemists because self-assembly is expected to be essential methodology to overcome the synthetic difficulties encountered in the preparation of highly complicated and ordered molecular systems.[1] Recently, we found a receptor based on a doubly bridged porphyrin molecule (trench porphyrin) which recognizes dialkyl tartrates selectively *via* four point hydrogen bonds.[2] The most important requirement for this system is the core conformations of the tartrate, *gauche* OH/OH and *anti* CO_2R/CO_2R, in which two carbonyl and two hydroxy oxygen atoms are practically planar. In contrast, the system is rather insensitive towards the properties of alkyl ester groups.[2] Thus, it is an interesting challenge to extend the system to a large scale assembly by modifying these alkyl moieties. We report here a self-assembling porphyrin trimer system consisting of two different types of porphyrin molecules and one tartrate derivative as a linker molecule.[3]

For this purpose, we designed a new tartrate linker molecule **1** which has two pyridine moieties arranged in a way so that the pyridine and tartrate moieties may act as independent recognition sites for the porphyrin molecules. Compound **1** was prepared by acid-catalysed reaction of l-tartaric acid with an excess of 3-(3′-pyridyl)propanol in toluene. The complex formation between **1** and *meso* trench porphyrin **2** was confirmed by UV–VIS spectroscopic titration showing a red shift of the Soret band of **2** (428 nm) with a clear isosbestic point, giving an association constant of 2300 ± 100 $dm^3 mol^{-1}$ at 288 K. ^1H NMR data (Table 1) reveal further details of the present complex formation. Upon complexation with **2**, two hydroxy and H_t protons (see Fig. 1) of **1** exhibit an unusual upfield shift as previously reported for simple alkyl tartrates.[2] The association constant is estimated to be $>1 \times 10^5$ $dm^3 mol^{-1}$ at 223 K. In contrast, the proton signals of the pyridyl moiety are observed in the normal aromatic region and show only a 0.1–0.3 ppm upfield shift upon complexation. These observations indicate that **1** complexes with **2** at the tartrate site *via* four hydrogen bonds and the pyridyl moieties practically remain free. Another porphyrin component of the present assembly, octaethylporphyrin Rh complex **3**, also forms a complex with **1** giving a stable 2 : 1 complex which is isolable giving *m/z* of 1729.77 in a FABMS spectrum (calc. for $C_{92}H_{113}N_{10}O_6Rh_2Cl_2$, *m/z* 1729.63). As shown in Table 1, the pyridyl protons of this complex are shifted upfield by 2.0–8.5 ppm with respect to those of free **1**, while the H_t protons show a relatively small upfield shift. The very large upfield shifts of H_c and H_d demonstrate the coordination of the pyridyl moieties of **1** on Rh atoms[4] and that the tartrate moiety does not directly participate in the complex formation. Thus, the tartrate and pyridyl moieties of **1** are confirmed to act as independent binding sites for porphyrins **2** and **3**. Based on these results, we attempted to construct a porphyrin trimer self-assembly. The ^1H NMR spectrum of the mixture of **1** (1.0 mm), **2** (1.0 mm) and **3** (2.0 mm) in $CDCl_3$ indicated that, at 223 K, no free pyridyl moieties of **1** were observed and new pyridyl signals (Table 1) appear in addition to those of the 2 : 1 complex of **3** and **1**. This behaviour is independent of the mixing sequences of the three components. It should be noted that both the tartrate and pyridyl moieties simultaneously show large upfield shifts which indicates the binding of the tartrate moiety on **2** and the pyridyl moiety on **3** respectively. Integration data for these protons gives the association constant between **2** and the 2 : 1 complex of **3** and **1** as 3000 ± 500 $dm^3 mol^{-1}$ at 223 K which is much smaller than that for **2** and **1**, while the pyridyl moieties of **1**

Table 1 ^1H NMR chemical shifts (δ) of **1** in $CDCl_3$ under various conditions[a]

	Tatrate moiety		Pyridyl moiety			
Host	H_t	OH	H_a	H_b	H_c	H_d
none	4.55	—[b]	7.51	7.22	8.44	8.45
2[c]	0.68	−3.81	7.22	7.15	8.45	8.20
	0.56	−4.13	7.24	7.08	8.38	7.89
3	2.70	4.00[d]	5.52	4.65	0.20	−0.06
2 + **3**[c,e]	0.02	−4.18	5.13	4.59	−0.15[f]	−0.48
	−0.18	−4.43	5.00	4.54		−0.73

[a] The data are obtained at 223 K except those of **1** (288 K). [b] Unclear. [c] Two signals are observed due to the unsymmetrical structure of **2**. [d] Owing to heavy overlap with the ethyl signals of **3**, the position is assigned from COSY data. [e] [**1**] = [**2**] = 1×10^{-3} m; [**3**] = 2×10^{-3} m. Under these conditions, *ca.* 60% of **2** forms the assembly with a 1 : 2 complex of **1** and **3**. [f] No separation for H_c was observed.

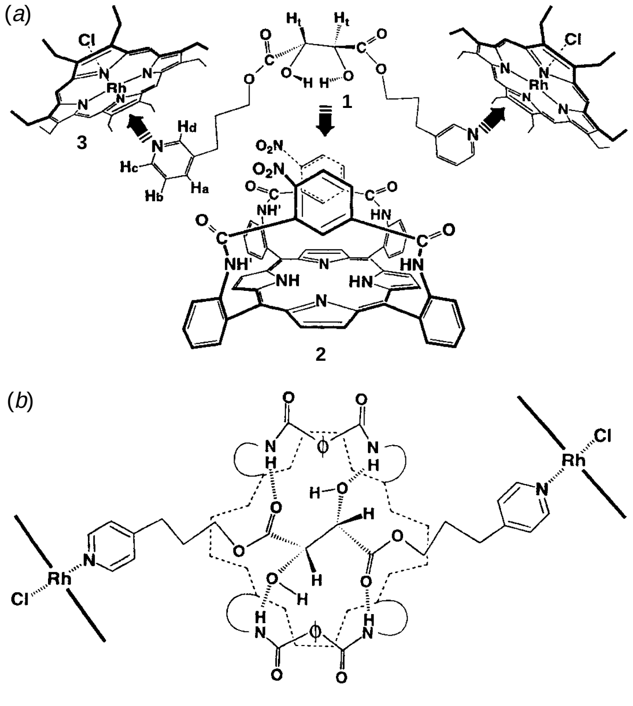

Fig. 1 Self-assembling porphyrin trimer system. (*a*) Component structures. (*b*) Schematic assembly structure.

quantitatively form complexes with **3** even under the present conditions. Although the smaller association constant suggests the existence of significant steric hindrance between the core porphyrin **2** and the two terminal porphyrins **3** due to the short alkyl chains of **1**, the results clearly indicate that the present system affords the quaternary self-assembly shown in Fig. 1 without any confusion between the different types of binding sites.

References

1 G. M. Whitesides, J. P. Mathias and C. T. Seto, *Science*, 1991, **254**, 1312; J. M. Lehn, *Science*, 1993, **260**, 1762; A. C. Bennist-on, A. Harriman and V. M. Lynch, *Tetrahedron Lett*., 1994, **35**, 1473; H. L. Anderson, S. Anderson and J. K. M. Sanders, *J. Chem. Soc., Perkin Trans. 1*, 1995, 2231; M. S. Goodman, V. Jubian, B. Linton and A. D. Hamilton, *J. Am. Chem. Soc*., 1995, **117**, 11 610; C. Valdes, U. P. Spitz, L. M. Toledo, S. W. Kubik and J. Rebek Jr., *J. Am. Chem. Soc.,* 1995, **117**, 12 733. J. P. Mathias, C. T. Seto, E. E. Simanek and G. M. Whitesides, *J. Am. Chem. Soc*., 1994, **116**, 1725; J. P. Collin, A. Harriman, V. Heitz, F. Odobel and J. P. Sauvage, *J. Am. Chem. Soc*., 1994, **116**, 5679; M. Fujita, S. Nagao and K. Ogura, *J. Am. Chem. Soc*., 1995, **117**, 1649; A. V. Chernook, A. M. Shulga, E. I. Zenkevich, U. Rempel and C. V. Borczyskowski, *J. Phys. Chem*., 1996, **100**, 1918.

2 Y. Kuroda, Y. Kato, M. Ito, J. Hasegawa and H. Ogoshi, *J. Am. Chem. Soc*., 1994, **116**, 10 338.

3 For porphyrin dimer system, see: C. M. Drain, R. Fischer, E. G. Nolen and J. M. Lehn, *J. Chem. Soc., Chem. Commun*., 1993, 243; Y. Kobuke and H. Miyaji, *J. Am. Chem. Soc*., 1994, **116**, 4111; J. L. Sessler, B. Wang and A. Harriman, *J. Am. Chem. Soc.,* 1995, **117**, 704; Y. Aoyama, T. Kamohara, A. Yamagishi, H. Toi and H. Ogoshi, *Tetrahedron Lett*., 1987, **28**, 2143; Y. Kuruoda, A. Kawashima, T. Urai and H. Ogoshi, *Tetrahedron Lett*., 1995, **46**, 8440.

4 H. Ogoshi, H. Hatakeyama, K. Yamamura and Y. Kuroda, *Chem. Lett*., 1990, 51.

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