Construction of porphyrin–cyclodextrin self-assembly with molecular wedge†

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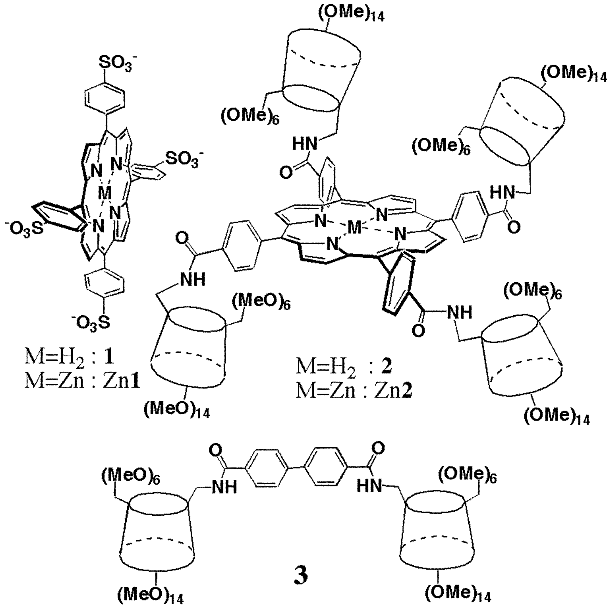
A new host porphyrin bearing four permethyl-β-cyclodextrin moieties for multi-porphyrin assembly forms a unique 2 : 2 assembly with the tetra-anion of tetrakis(*p*-sulfonylphenyl)porphyrin (TPPS) in aqueous solution.

Several research groups have reported the complexation of ionic tetraphenylporphyrin derivatives with *O*-methylated cyclodextrins.[1] Among these investigations, Kano *et al.* recently examined the detailed mechanism of highly specific 2 : 1 complex formation between heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin (TMCD) and various cationic or anionic porphyrins.[2] The binding constants in water are probably too high to be determined with an acceptable accuracy by the methods employed here, but not in general, which indicates practically quantitative complex formation between TMCD and the charged porphyrin in the host–guest concentration range of 10^{-6}–10^{-7} M. These unique characteristics of the TMCD-charged porphyrin systems suggest an interesting possibility for construction of porphyrin assemblies where the porphyrin molecules act as not only photochemical and/or redox elements but also as molecular wedges which tightly unite each cyclodextrin framework in the assemblies. In this work we describe a unique multi-porphyrin assembly formed in an aqueous solution *via* specific interaction between the tetra-anion of tetrakis(*p*-sulfonylphenyl)porphyrin (**1**) and TMCD derivatives.

The main framework of the assembly is the tetraphenylporphyrin derivative bearing four TMCD moieties (**2**), which is synthesized by the condensation reaction of tetrakis(*p*-chloroformylphenyl)porphyrin with per-*O*-methyl-6-amino-β-cyclodextrin.[3] The complex formation between **1** and **2** is examined by visible spectroscopic titration shown in Fig. 1a. In order to extract more useful information from the present rather complex spectroscopic change due to the strong absorption of titrant **2**, the following mathematical treatment of the spectra [eqn. (1)] was carried out for the observed spectra (see ESI for details).

$$\Delta\text{Abs}(\lambda) = \text{Abs}(\lambda)_{\text{obs}} - \varepsilon_1(\lambda)[\mathbf{1}]_{\text{Total}} - \varepsilon_2(\lambda)[\mathbf{2}]_{\text{Total}} \quad (1)$$

The resultant difference spectra (ΔAbs) given in Fig. 1b show very interesting characteristics in that the spectra hold clear isosbestic points which are identical with those observed for 1 : 2 complex formation of **1** with unsubstituted TMCD (Fig. 1b). The results strongly suggest the following important characteristics of the present complex formation: a) stoichiometry of the present complex formation seems to be 1 : 1 (inset of Fig. 1b), b) the environment around **1** in the **1·2** complex is practically the same as that in **1**·TMCD$_2$, c) the spectrum of **2** is practically unaffected by complexation with **1**. The apparent binding constant obtained from the spectral changes is evaluated to be larger than 2.3×10^8 M^{-1}.‡ Although the stoichiometry is easily measured by the usual Job's plot analysis, the latter two results are unexpected and contradict the straightforward 1 : 1 binding model as obtained by the simple Job-type analysis, because simple consideration of the molecular models indicates that the short amide arms in **2** connecting porphyrin and TMCD moieties do not allow the formation of any 1 : 1 complex having the structure of the reported **1**·TMCD$_2$ without serious distortion of **2**. Thus, these results seem to indicate an *n* : *n*



M=H$_2$: **1**
M=Zn : Zn**1**

M=H$_2$: **2**
M=Zn : Zn**2**

3

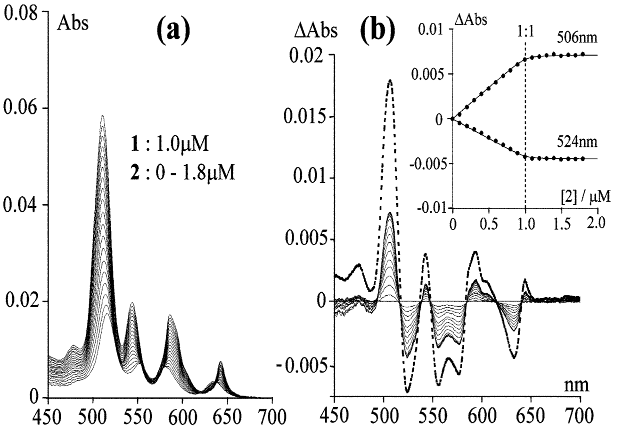


Fig. 1 The titration spectra of **1** with **2** at pH 9.0: a) observed spectral change of the Q-band region; b) different spectra calculated according to eqn. (1) (solid line) and the corresponding different spectrum of **1**·TMCD$_2$ (dashed line, [**1**·TMCD$_2$] = 2.5×10^{-6} M). Inset: the titration curves at 506 and 524 nm, where the theoretical lines are generated by using $K_{\text{app}} = 2.3 \times 10^8$ M^{-1}.

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† Electronic supplementary information (ESI) available: synthesis and spectroscopic data of the new host **2**, detailed mathematical treatment of spectra, detailed calculation of center-to-center distance between porphyrins, Job's plot data for complexation between **1** and **2**, SAXS data, GPC data, and ESI mass spectra for **1·2** and **1·3** complexes. See http://www.rsc.org/suppdata/cc/b3/b311079f/

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complex, $\mathbf{1}_n\cdot\mathbf{2}_n$, rather than simple **1·2**. In order to evaluate the value of *n*, estimation of the molecular dimensions of the present complex was attempted by the methods of gel permeation chromatography (GPC) and small angle X-ray scattering (SAXS). The molecular weight estimated by GPC is 1.5×10^4 Da and the molecular size calculated from the SAXS data is a short cylindrical shape of 20 Å height and 20 Å radius (see ESI). Both results strongly indicate the structure of $\mathbf{1}_2\cdot\mathbf{2}_2$ as shown in Fig. 2. In this model, it is clear that no porphyrin structure suffers from serious strain and/or steric hindrance on complexation and the porphyrin–porphyrin distances are large enough to result in no appreciable electronic interaction between them. Similar 1 : 1 complex formation is observed for combination of Zn complexes of **1** and **2**, where all combinations, **Zn1/2**, **Zn2/1** and **Zn1/Zn2**, show binding constants larger than 8×10^7 M^{-1}. Interestingly, in the case of heterogeneous combination of porphyrin components, irradiation of the Zn porphyrin results in significant fluorescence quenching of the Zn component and enhancement of the fluorescence of the free-base component as shown in Fig. 3a, indicating 81% energy transfer from **Zn1** to **2** (e.t. I in Fig. 2).§ Further analogous information on the present unique complexation using **1** as a molecular wedge fixing two TMCD moieties is obtained from examination of the binding behaviour of another cyclodextrin dimer **3**.[4]

The cyclodextrin dimer **3** also shows similar 1 : 1 complex formation with **1** or **Zn1** ($K > 1.3 \times 10^8$ M^{-1}). The molecular weight of this complex estimated by GPC is 7.3×10^3 Da indicating formation of the $\mathbf{1}_2\cdot\mathbf{3}_2$ type complex again. Furthermore, negative mode ESI mass spectroscopic investigation for the assembly of **1** and **3** shows the existence of $(\mathbf{1}_2\cdot\mathbf{3}_2)^{7-}$ and $(\mathbf{1}_2\cdot\mathbf{3}_2)^{5-}$ ions as well as the major $(\mathbf{1}\cdot\mathbf{3})^{4-}$ ion, even though the signal is rather minor due to the experimental restriction that the sample must be dissolved in aqueous 45% methanol solution which markedly reduces the binding ability of the present cyclodextrin dimer.¶ The most interesting observation is that the aqueous solution of the ternary mixture of **1**, **Zn1** and **3** (pH 9.0, [**1**] = [**Zn1**] = 1.0×10^{-6} M, [**3**] = 2.0×10^{-6} M) also shows energy transfer from **Zn1** to **1**, of which the apparent energy transfer efficiency is 26% as shown in Fig. 3b. Since the solution of **1** and **Zn1** without **3** shows no such energy transfer behaviour even in the presence of TMCD, the observed energy transfer indicates the formation of a 1 : 1 : 2 assembly of **1**, **Zn1**, and **3**. All these results indicate the formation of 2 : 2 assemblies composed of the host molecules and the porphyrin components. Furthermore, the ternary mixture of **1**, **Zn1** and **3** actually gives the 1 : 1 : 2 ternary assembly where there is significant energy transfer from **Zn1** to **1** such as the e.t. II process shown in Fig. 2, though the formation of the heterogeneous ternary assembly and 2 : 2 binary assemblies such as $\mathbf{1}_2\cdot\mathbf{3}_2$ or $(\mathbf{Zn1})_2\cdot\mathbf{3}_2$ is simply a statistical process.

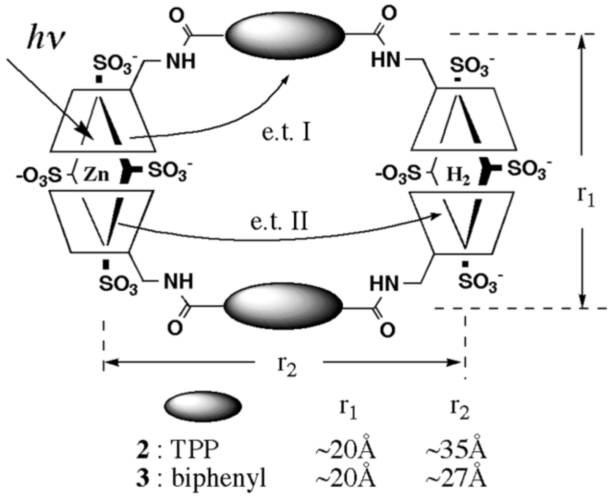

Fig. 2 Possible structure of 2 : 2 complex and the porphyrin–porphyrin distances estimated from the corresponding molecular models.

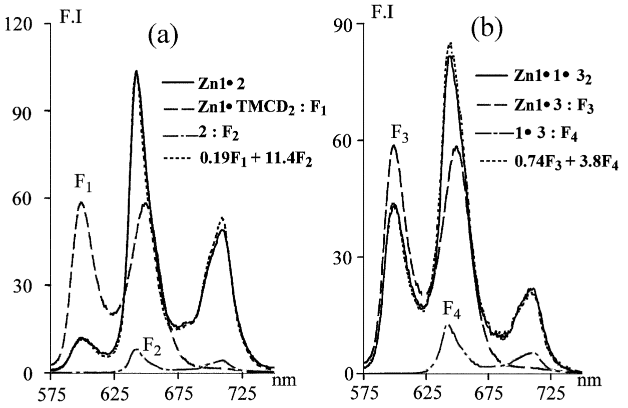

Fig. 3 Fluorescence spectra of the assemblies constructed with heterogeneous porphyrin combination (pH 9.0). The solid lines are the observed fluorescence spectra of the assemblies, a) $(\mathbf{Zn1})_2\cdot\mathbf{2}_2$ at λ_{ex} = 555 nm and b) $\mathbf{Zn1}\cdot\mathbf{1}\cdot\mathbf{3}_2$ at λ_{ex} = 561 nm. The spectra F_1, F_2, F_3, and F_4 are the fluorescence spectra of the corresponding assembly components and the dashed lines are the simulated spectra reconstructed according to the given combination.

Notes and references

‡ Since completion of the complex formation is observed practically at the 1 : 1 stoichiometric point as shown in the titration curves of Fig. 1, the calculated binding constant is expected to contain large errors and should be considered to be the minimum value.

§ Assuming a Förster mechanism and using spectroscopic data and quantum yield of **Zn1**, the observed energy transfer efficiency corresponds to 20 Å center-to-center separation between the donor–acceptor porphyrins (for details, see ESI).

¶ The apparent binding constant for complexation between **1** and **3** is 3×10^4 M^{-1} in aqueous 45% methanol solution.

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