

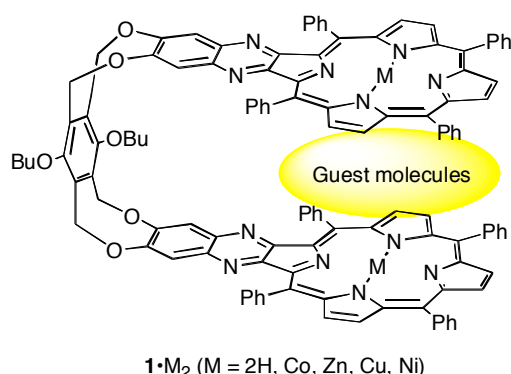
SYNTHESIS OF MOLECULAR TWEEZERS BEARING TWO PORPHYRINS AND ITS COMPLEXATION TOWARD ELECTRON ACCEPTORS

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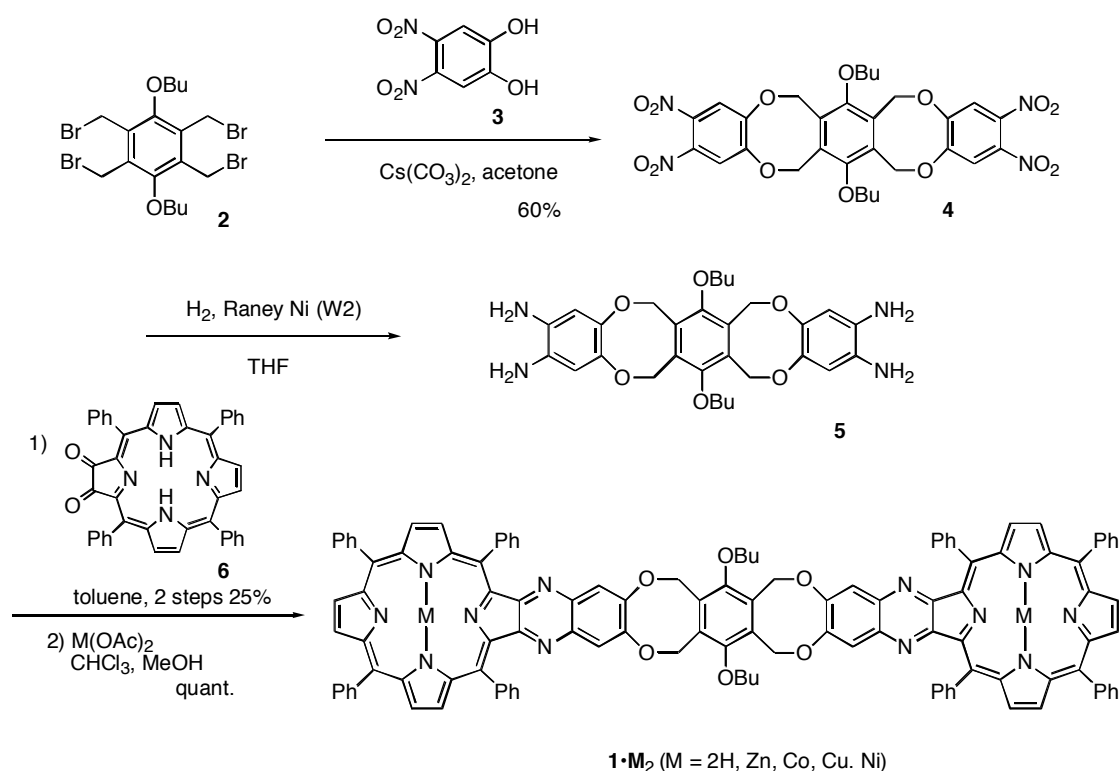
Abstract – Synthesis of new flexible molecular tweezers $\mathbf{1}\cdot\mathbf{M}_2$ ($\mathbf{M} = 2\mathbf{H}, \text{Co}, \text{Zn}, \text{Cu}, \text{Ni}$) based on bis-dioxo[2.2]orthocyclophane bearing two porphyrins is presented. The molecular tweezers ($\mathbf{1}\cdot(2\mathbf{H})_2$) can bind not only planar π -electron acceptors, such as tetracyanoquinodimethane (TCNQ) and tetracyanobenzene (TCNB) but also a spherical guest C_{60} .

Recognition of planar molecules by non-covalent interaction is an interesting topic in host-guest chemistry in order to understand the effects of π - π stacking interactions. Cleft molecules,¹ which have two aromatic chromophores connected by a spacer, are suitable receptors for planar π -electron guests, since they can hold the guest with the two aromatic arms through the π - π stacking interactions. In our previous work,² we have demonstrated that the flexible structure based on bis-dioxo[2.2]orthocyclophane can bind π -electron acceptors such as tetracyanoquinodimethane (TCNQ) and tetracyanobenzene (TCNB), because the two terminal aromatic rings take tweezers-type arrangement with face-to-face orientation, which is suitable for π - π stacking interactions. It is well known that porphyrin has an extended π -electron surface, and also interesting properties such as molecular transfer, oxidation catalyst and electron transfer. These characters have been stimulating chemists to investigate host-guest chemistry using porphyrin. While the stacking interaction of aromatic compounds with synthetic porphyrins in aqueous media is extensively documented,³ it is rather limited in organic media.⁴ In this paper, we wish to report the new molecular tweezers ($\mathbf{1}\cdot\mathbf{M}_2$) bearing two metalloporphyrins at their termini, which shows binding affinity toward not only planer electron acceptor guests but also a spherical guest, C_{60} .⁵

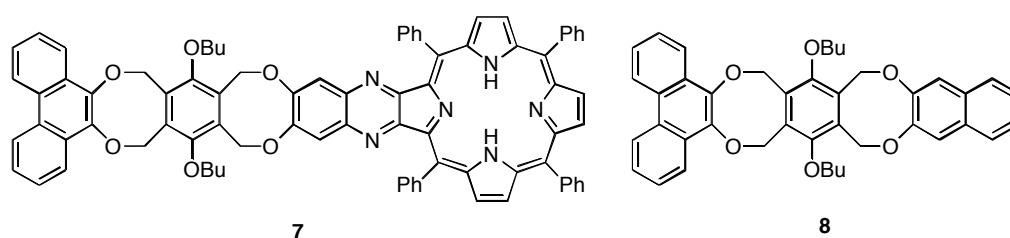


Figure

The synthesis of the host molecule ($1 \cdot M_2$) is shown in Scheme 1. Inter- and intra-molecular Williamson etherification of 4,5-dinitroprocathecol (**3**)⁶ with 1,4-dibutoxy-2,3,5,6-tetrakis(bromomethyl)benzene (**2**)⁷ by treatment with Cs_2CO_3 in acetone give tetranitro compound (**4**) in 60% yield. Reduction of four nitro groups of **4** to amino groups with Raney-Ni(W2) under hydrogen atmosphere afforded tetraamine compound (**5**), which was unstable under atmospheric conditions, and therefore it was used to the next step without further purification. Condensation of **5** with tetraphenylporphyrin-2,3-dione (**6**)⁸ afforded desired host molecule **1** in 25% yield over two steps. Corresponding metalloporphyrins were quantitatively obtained by treatment of **1** with excess amounts of the metal acetates in DMF, respectively.⁹ The reference compounds (**7**) and (**8**) were also prepared by the similar procedure for comparison.¹⁰



Scheme 1



Scheme 2

As shown in Figure 1, standard titration experiments between $\mathbf{1} \cdot (2\text{H})_2$ and TCNB were carried out by ^1H -NMR spectroscopy in CDCl_3 . The signal of the proton of TCNB shifted upfield when host molecule ($\mathbf{1}$) was added to the guest solution, indicating that TCNB was influenced by porphyrin's ring current of the host molecule. The non-linear curve fitting analysis of the complexation induced up-field shift data of the TCNB proton gave an association constant ($160 \pm 4 \text{ M}^{-1}$) and a complexation-induced chemical shift change $\Delta\delta$ of the protons ($1.02 \pm 0.02 \text{ ppm}$) in the completely bound guest using damping Gauss-Newton algorithm with a 1:1 binding stoichiometry (Table 1).¹¹ Similarly, an association constant and a complexation-induced chemical shift were obtained from titration experiments using TCNQ as the guest molecule.

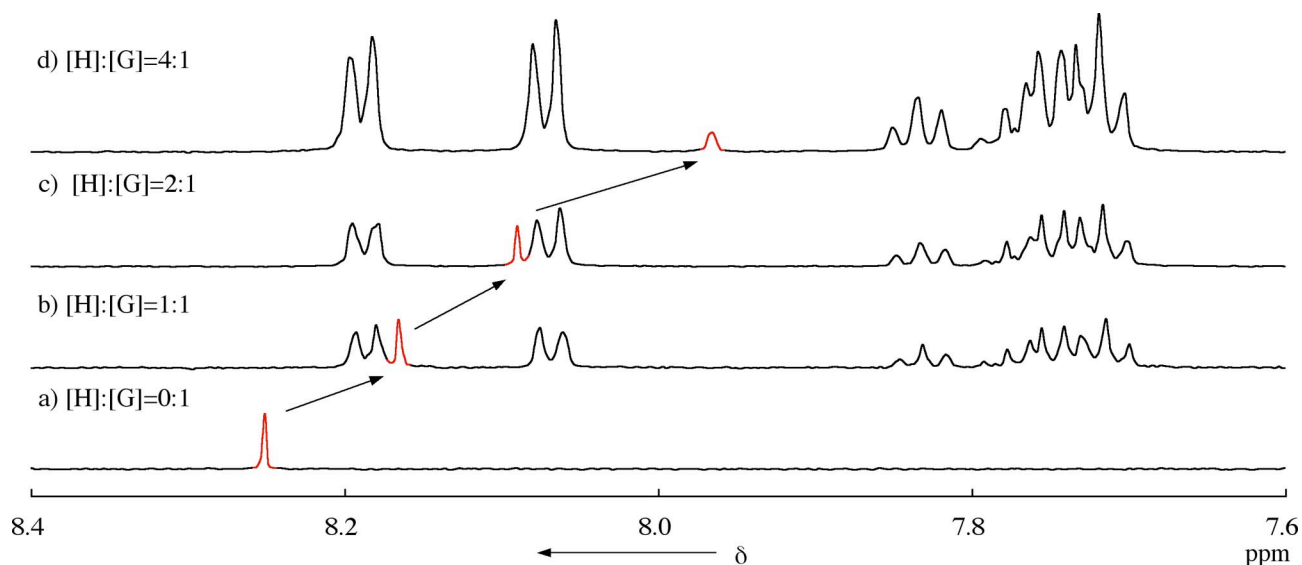


Figure 1. Partial (aromatic region) ^1H NMR spectra (500 MHz) recorded in CDCl_3 at 298 K of a) TCNB (1.0 mM), b) TCNB (1.0 mM) and 1.0 equiv host, c) TCNB (1.0 mM) and 2.0 equiv host, and d) TCNB (1.0 mM) and 4.0 equiv host.

In order to examine the contribution of porphyrin ring for host-guest complexation, mono-porphyrin host molecule ($\mathbf{7}$) and non-porphyrin host ($\mathbf{8}$) were used as reference compounds, and the binding constants and the complexation-induced chemical shifts of TCNB and TCNQ were obtained in the same way (Table 1). $\mathbf{1} \cdot (2\text{H})_2$ has larger binding constants and larger complexation-induced chemical shifts toward TCNB and TCNQ when compared to those of $\mathbf{7}$. While the induced shifts of the guest are too small to obtain binding constant of $\mathbf{8}$, small up-field shift was shown when the excess amount (10 eq.) of the host

was added to the guest solution.¹² These results suggest that two porphyrin rings play an important role in grasping the planar π -electron acceptor guests in solution phase.

Table 1. Association constants K (M^{-1}) and complex induced chemical shifts $\Delta\delta$ (ppm) of host molecules with π -electron accepting guests^a

	Host	1 •(2H) ₂	7	8
TCNB	$K(M^{-1})$	160 \pm 4	140 \pm 20	^b
	$\Delta\delta$	1.02 \pm 0.02	0.29 \pm 0.02	0.121 ^c
TCNQ	$K(M^{-1})$	114 \pm 2	71 \pm 10	^b
	$\Delta\delta$	0.76 \pm 0.01	0.32 \pm 0.04	0.058 ^c

(a) Measured by ¹H NMR spectroscopic titration in CDCl₃ at 298 K. (b) It is impossible to determine the association constants due to the very small interactions between **3** and guest molecules. (c) These values were obtained under the condition [H]/[G]=10.

It is well known that fullerenes are weak electron acceptors with curved surface. This character attracted much attention and the complex formation of fullerenes with porphyrins and/or metalloporphyrins was studied.¹³ Especially, Aida's host¹⁴ binds the fullerene strongly. It has an ideal parallel arrangement of two porphyrins with 12 Å separation when bound to C₆₀. On the other hand, our host has a shorter interplanar distance (*ca.* 6.5 Å) when it has a cleft type conformation. It would be too small to bind C₆₀. However, the spacer unit of the host, dioxo[2.2]orthocyclophane has a good flexibility for adjusting to the larger guest molecules.

In order to estimate the binding abilities of the host molecule toward C₆₀, titration experiments were carried out with UV spectroscopic method. When C₆₀ was added to free base **1**•M₂ solution in toluene at 25 °C, isosbestic points were observed at 420 and 468 nm, and the Soret absorption band showed a clear red shift with a decrease in absorbance. From the observed spectral change profiles, the association constants were evaluated as shown in Table 2. This titration showed the following trend for fullerene binding: 2H > Co > Zn > Cu > Ni. Although the association constants are much smaller than those of the Aida's host, the binding trend to C₆₀ is very similar. In order to bind the large spherical guest, the molecular tweezers should widen the interplanar separation of the two terminal porphyrins from the rather strain-free parallel arrangement to a tilted form as has been found in the Boyd's Pd-linked porphyrin dimers.¹⁵ It can be easily attained by changing the conformation of one of the two dioxo[2.2]orthocyclophanes, the hinge part of the host, from the rather strain-free twist boat to a chair form. A modeling study¹⁶ suggested the inclination of one of the porphyrin rings by 38° with respect to the other with the chair conformation of one of the hinges of the host. The tilted arrangement of the porphyrins shifts the nearest contact point to C₆₀ guest from the ideal centroid of the porphyrin toward

the hinge part to some extent. This might decrease the attractive interaction between the terminal porphyrin rings and the C₆₀ guest.

Table 2. Association constant K (M⁻¹) of metalloporphyrin dimmers 1•M₂ with C₆₀^a

M	2H	Co(II)	Zn(II)	Cu(II)	Ni(II)
K(M ⁻¹)	940 ± 30	740 ± 20	650 ± 20	480 ± 40	280 ± 40

(a) Measured by UV-VIS spectroscopic titration in toluene at 298 K.

The binding constants of 1•M₂ to the C₆₀ guest are very similar to those of the Boyd's hosts having a similar tilted arrangement of the two porphyrins. These results support the idea that the two porphyrins of 1•M₂ have the tilted arrangement in the complexes with C₆₀.

In conclusion, the host molecule (1•M₂) can bind not only planer π-electron acceptor guests such as TCNB and TCNQ, but also the large non-planar π-electron guest, C₆₀ in organic media. These results would give us further information for π-π interaction of porphyrin.

ACKNOWLEDGEMENTS

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