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ABSTRACT

For the continuing study of the molecular recognition of the π -electron-poor host comprised of two pyromellitic diimides and two dialkoxynaphthalenes, its inclusion with π -electron-rich polymethoxybenzenes has been examined. The UV-vis titration studies indicated following order of the association constants (K_a 's) as 1:1 complexes in CHCl₃: 1,3,5-trimethoxybenzene (31.3 M⁻¹)>1,3-dimethoxybenzene (9.2 M⁻¹)>1,2-dimethoxybenzene (6.5 M⁻¹)>1,4-dimethoxybenzenes (2.8 M⁻¹). The X-ray structural analysis of the complexes between the host and dimethoxybenzenes proved the intracavity 1:1 complexes and provided useful information on the structures of the complexes. Not only charge transfer interactions but also other weak interactions such as electrostatic, van der Waals, and the unique hydrogen bonds between the α -hydrogen atoms of the naphthalene and the methoxy oxygen atoms were considered to be responsible for the magnitude of the K_a 's. Thus molecular recognition of polymethoxybenzenes has been accomplished by the neutral host using multipoint weak interactions in an organic solvent.

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1. Introduction

Pyromellitic diimide represents the smallest homolog of the aromatic diimide and it has been used as important components in supramolecular chemistry due to its π -accepting ability and flat π plane.¹ The electrochemical properties of pyromellitic diimide play an important role in the functionality of the supramolecular architectures such as [2]catenanes,² [2]rotaxanes,³ and molecular receptors.⁴ In our continuing efforts to synthesize organic molecular tubes with the diameter of 1–5 nm for the inclusion of organic guests, we have designed and synthesized the hosts 1, 2, and 3 comprised of pyromellitic diimide moieties with electron accepting properties and intervening dialkoxybenzene or naphthalene spacers as structural units of the tubes (Fig. 1).⁵ Their host cavities are π -electron-poor and preferential inclusion of the π -donating aromatic guests is expected via charge transfer (CT) interactions as one of the driving force of the inclusion. Pyromellitic diimide is a suitable skeleton of the structural unit because it has four connection sites; two nitrogen atoms for the construction of the structural units and the two carbon atoms at the 3,6-positions of the benzene ring of the pyromellitic diimide for the connection of the structural units. The molecular tubes constructed by the connection of the structural units at the 3,6-positions of the pyromellitic diimide should have an electron-deficient long cavity, in which one-dimensional array of the π -donating aromatic guests may be formed. Therefore our molecular tubes may contribute to the development of new cluster chemistry of the aromatic π -donating molecules.

Previously, we found that the host **3** with three pyromellitic diimide moieties includes an electron-donating guest, [2.2.2]paracyclophane, via three-point CT interactions.^{5a} The host **2** with the two diimide moieties and benzene spacers interacts only outside of the cavity with electron-donating naphthols to form supramolecular assemblies via a combination of hydrogen bonds and CT interactions because of its small cavity size.^{5b} The homologous host **1** with naphthalene spacers includes an aniline in the cavity by CT interaction. In addition, the amino group of this aniline further interacts with anilines outside of the cavity to form a cyclic aniline trimer in a void space by N–H…N and N–H… π interaction in the solid state.^{5c} This unexpected structure of the inclusion complex prompted us to study the inclusion phenomena of **1** in more detail and we found that **1** can recognize polymethoxybenzenes in CHCl₃.

In the past two decades, several recognition studies of polymethoxybenzenes by artificial macrocyclic hosts have been reported.⁶ Stoddart et al. reported the molecular recognition of the 1,2-, 1,3-, and 1,4-dimethoxybenzenes (K_a 8.1, 8.0, and 17 M⁻¹) using



^{*} Molecular Tubes and Capsules, Part 5. For Part 1–4, see Refs. 5a–d.

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Figure 1. Three pyromellitic diimide-based macrocycles 1, 2, and 3 and their CPK presentations.

a tetracationic host, cyclobis(paraquat-*p*-phenylene), in CH₃CN, and elucidated the crystal structures of the inclusion complexes of the 1,4- and 1,2-dimethoxy-benzenes.^{6a,b} Fujita et al. accomplished the molecular recognition of 1,3,5-trimethoxybenzene (K_a 30, 580, and 330 M⁻¹) by the macrocyclic polynuclear complex [(en)Pd(4,4'-bpy)]₄(NO₃)₈, in water.^{6c} Diederich et al. studied the inclusion phenomena of octamethoxy-substituted tetraoxa[n.1.n.1]cyclophanes (n=3 or 4) and determined the K_a 's for 1,4-dimethoxybenzene in water (n=4, K_a 1.02×10⁴ M⁻¹; n=3, K_a 3.7×10² M⁻¹) and in MeOH (n=4, K_a 8 M⁻¹).^{6d} These results suggested the importance of hydrophobic interaction for the effective molecular recognition of di- and trimethoxybenzenes.

In the present study, investigation of the inclusion properties of the hosts as structural units of the molecular tubes is of primary importance and we wish to report here the structural and the electrochemical properties of the host **1**, and its inclusion phenomena of polymethoxybenzenes. We found that uncharged neutral host **1** can recognize polymethoxybenzenes in nonpolar organic solvent via multiple weak interactions such as CT, electrostatic, van der Waals, and C–H···O hydrogen bonding interactions.

2. Results and discussion

2.1. Synthesis

In the previous communication, we reported the coupling reaction of pyromellitic dianhydride with 2,2-bis(aminomethyl)-3,6dihexyloxynaphthalene $\mathbf{8}$.^{5c} We describe here the synthesis of the diamine $\mathbf{8}$ and the coupling products $\mathbf{1}$ and $\mathbf{9}$ (Scheme 1). The diamine **8** was synthesized from 2,7-dihydroxynaphthalene **4** by bromination⁷ and alkylation of the hydroxyl groups of **5** with hexyl bromide,⁸ followed by replacement of the bromine atoms of **6** with cyano groups and their reduction with DIBAL in toluene. The resultant amine **8** was used for the next coupling reaction without further purification. The amine **8** was reacted with the pyromellitic dianhydride in THF at room temperature, and then the reaction mixture was stirred at 50 °C for 31 h. The resultant amic acids were dehydrated with Ac₂O and AcONa at 100 °C and the crude products were separated by silica gel column chromatography with CHCl₃ to give the macrocycles **1** (13%) and **9** (9%), respectively.^{5c}

2.2. Structural properties

We previously reported the molecular structure of the complex $1 \cdot (aniline)_7$ in the solid state,^{5c} which showed that the transannular pyromellitic diimide π -faces were located parallel to each other with the average transannular distance of ca. 7.3 Å, and the two naphthalene rings were coplanar and perpendicular to the pyromellitic diimide π -faces (Fig. 2). In solution, the rotation of the diimide moieties and the flipping of the naphthalene rings were expected. The variable temperature (VT) ¹H NMR spectra of **1** in CD₂Cl₂ showed a gradual broadening of the signals assigned to the diimide H_a protons, naphthalene H_b and H_c protons, and methylene protons H_d as the temperature was lowered, but the coalescence of these signals was not observed down to 193 K (Fig. 3), suggesting the mobility of 1 even at 193 K as expected. MO calculations (B3LYP/6-31G*) suggested that the parallel-conformer is more stable than the *syn*-one by 1.71 kcal/mol (Fig. 4),⁹ whereas the possible anti-one, in which two naphthalene rings are located in the



Scheme 1. Synthesis of pyromellitic diimide-based macrocycles 1 and 9.

opposite positions, is less stable than the *syn*-one and it is not the stable conformer with a local minimum energy. Thus the *parallel*-conformer was predicted to be the most stable and the conformations of $\mathbf{1}$ in the solid state were all *parallel*-ones.¹⁰ The crystal

packing force may also contribute to the stability of the *parallel*-conformation to some extent.

2.3. Electrochemical properties

The cyclic voltammetric traces of **1** and **2** were recorded in a 1,2dichlorobenzene solution in the presence of n-Bu₄NPF₆ as the supporting electrolyte (Fig. 5, Table 1). The host **2** with the transannular distance of two diimide π -faces being ca. 5.0 Å exhibited the first two-electron reduction followed by the second two-



Figure 2. Crystal structure of the clathrate between 1 and aniline. The anilines outside of the cavity of 1 were omitted for clarify.



Figure 3. The VT ¹H NMR spectra of 1 in CD_2Cl_2 (5×10⁻³ M, 500 MHz).



Figure 4. Two optimized structures of 1' based on MO calculation (Gaussian 03, B3LYP/6-31G*). The hexyloxy groups were converted to methoxy groups along with a sketch of the anti-conformer.



Figure 5. Cyclic voltammograms of **1** (blue line) and **2** (red line): (a) CV trace from -0.5 to -3 (potential/V vs Fc/Fc⁺), (b) CV trace from -0.5 to -2.0 (potential/V vs Fc/Fc⁺).

Table 1	
Potential (V vs Fc/Fc ⁺) for reduction processes of ${\bf 1}$ and ${\bf 2}$	

	redE1	redE2	redE3	redE4	${}^{1}E_{1/2}$
1	-1.43	-1.51	-2.03	-2.13	-1.31
2	-1.42		-2.25	-2.41	-1.29

All electrochemical measurements were performed in *o*-dichlorobenzene solution $(5 \times 10^{-4} \text{ M})$ containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate at the scan rate of 200 mV s⁻¹.

electron reduction and each reduction process was split into two waves (E1 -1.42; E2 -1.51 V and E3 -2.25; E4 -2.41 V vs Fc/Fc⁺). Although no splitting was observed in the first two-electron reduction in **1** (*E*1 and *E*2 1.43 V vs Fc/Fc⁺) with the transannular distance of two diimide π -faces being ca. 7.3 Å, the splitting of the second two-electron reduction (E3 -2.03; E4 -2.13 V vs Fc/Fc⁺) was observed. Pyromellitic diimide shows two reversible oneelectron reductions and the first and second waves are ascribed to the radical anion and dianion species, respectively.^{2f,3d,11} The splitting of the first two-electron reduction in 2 indicated the electronic repulsion between radical anion species and neutral species, and the splitting of the second two-electron reduction in 1 and **2** indicated the presence of the electronic repulsion between radical anion species and dianion species (Fig. 6). These repulsive interactions may be more significant in 2 than in 1 as evidenced by the splitting of the first two-electron reduction and the negative shifts of the reduction potentials E2, E3, and E4 of 2 than the corresponding reduction potentials of 1 because of the shorter transannular distance between the imide π -faces in **2** than in **1**. These results indicated that the electronic repulsion between a neutral and a radical anion species of the diimide moieties would exist within ca. 5.0 Å, while that between a radical anion and a dianion species of the diimide moieties would be more significant and the interaction may exist even at ca. 7.3 Å. To the best of our knowledge, this is the first report of the effective distances of electronic interaction between a radical anion and a dianion species of transannular pyromellitic diimide moieties. The first half-wave potentials $({}^{1}E_{1/2})$ of **1** and **2** were almost the same, indicating the



Figure 6. Proposed reduction processes of 1 and 2.

similar LUMO energy levels in 1 and 2; i.e., the π -accepting ability is almost the same in 1 and 2.¹²

2.4. Inclusion properties

In the ¹H NMR titration study of **1** with 1,3-dimethoxybenzene in CDCl₃, the gradual upfield shift ($\Delta\delta$ –0.23 ppm) of the aromatic proton signal H_a of the diimide moieties and the corresponding downfield shift ($\Delta\delta$ 0.21 ppm) of the inner naphthalene proton signal H_b were observed by addition of 10 M equiv of the guest, while the outer naphthalene proton signal H_c remained intact (Fig. 7). These complexation shifts suggested the internal binding of the guest in a parallel fashion.

On the other hand, the negligible ¹H NMR complexation shift of the H_{a'} proton signal of **2** ($\Delta\delta$ –0.01 ppm) was ascribed to the external binding (Fig. 8). Previously we reported that the K_a value obtained by the UV-vis titration method between 2 and 1,4dimethoxybenzene was 0.3 M^{-1} in CHCl₃ and the small K_a value was ascribed to the external binding because of the small cavity size.^{5b} The K_a values of **1** with other polymethoxybenzenes were obtained by the UV-vis titration method since the ¹H NMR complexation shifts of polymethoxybenzenes were small except for 1,3,5-trimethoxy- and 1,3-dimethoxybenzenes. By employing the CT band as a quantitative spectroscopic probe and then subjecting the data to a Benesi-Hildebrand treatment, the 1:1 stoichiometry was established and the K_a values were obtained in CHCl₃ as is summarized in Tables 2 and 4.^{13,14} As a typical example, the CT spectral changes as an addition of the increasing amounts of 1,3dimethoxybenzene to 1 in CHCl₃ was shown in Figure 9a along with

the similar experiment between **2** and 1,3-dimethoxybenzene, in which only external binding was possible (Fig. 9b). A wide range of the K_a values between **1** and the polymethoxybenzenes was obtained $(1.6-31.3 \text{ M}^{-1})$ and 1,3,5-trimethoxybenzene showed the largest K_a value (31.3 M^{-1}) , which was comparable to that obtained by the ¹H NMR titration in CDCl₃ $[32.1\pm5.15 \text{ M}^{-1} (R=0.999)]$ by using nonlinear curve fitting with the 1/1 model (**1**: $1 \times 10^{-3} \text{ M}$). Although the internal and external bindings could not be distinguished by the UV–vis titration study, the K_a value of 0.3 M^{-1} for the external binding between **2** and dimethoxy- and 1,3,5-trimethoxybenzenes suggested that the contribution of the external binding to the K_a value was quite small.

The π -donating abilities estimated by the wavelength of the CT bands (λ_{CT}) and oxidation potentials (E_{ox}) of dimethoxybenzenes are in the order of 1,4-dimethoxybenzene>1,2-dimethoxybenzene \approx 1,3-dimethoxybenzene (Table 3),¹⁵ whereas the K_a values of **1** with dimethoxybenzenes in CHCl₃ are in the following order: 1,3-dimethoxybenzene (9.2 M⁻¹)>1,2-dimethoxybenzene ($(5.5 \text{ M}^{-1})>1,4$ -dimethoxybenzene (2.8 M^{-1}) (Table 4). This disagreement between the order of the magnitude of the CT interaction and that of the K_a values suggested the presence of other weak interactions. In order to obtain more detailed information on the structures of the complexes and elucidate the difference of the K_a values in dimethoxybenzenes, crystal structures of the complexes were investigated by the X-ray structural analysis.

The ORTEP drawings and space filling representations as well as the top views of the structures of 1,2-dimethoxybenzene@1, 1,3dimethoxybenzene@1, and 1,4-dimethoxybenzene@1 are shown in Figures 10 and 11. In all complexes, one guest molecule was



Figure 7. ¹H NMR spectra (300 MHz) of 1 in CDCl₃ at 5×10⁻³ M in the presence of 0–10 equiv of 1,3-dimethoxybenzene.



Figure 8. ¹H NMR spectra (300 MHz) of 2 in CDCl₃ at 5×10⁻³ M in the presence of 0–10 equiv of 1,3-dimethoxybenzene.

Table 2Association constants K_a 's between 1 or 2 and guest molecules in $CHCl_3$ (298 K)

Guest compounds	$K_{a} (M^{-1})$	
	1	2
1,2-Dimethoxybenzene	6.5±0.2	0.3±0.07
1,3-Dimethoxybenzene	9.2±0.02	$0.3 {\pm} 0.04$
1,4-Dimethoxybenzene	2.8±0.1	$0.3{\pm}0.03^a$

^a The association constant was reported in Ref. 5b.



Figure 9. (a) Absorption spectra of **1** in CHCl₃ $(1 \times 10^{-3} \text{ M})$ in the presence of 0–500 equiv of 1,3-dimethoxybenzene. (b) Absorption spectra of **2** in CHCl₃ $(1 \times 10^{-3} \text{ M})$ in the presence of 0–1500 equiv of 1,3-dimethoxybenzene.

Table 3

The oxidation potentials of the guest molecules and the maximum absorption wavelength of the CT bands of the CT complexes between **1** and the guest molecules

Guest compound	$E_{\rm ox}$ (V vs Fc/Fc ⁺) ^a	$\lambda_{CT} (nm)^{b}$
1,2-Dimethoxybenzene	1.15	383
1,3-Dimethoxybenzene	1.15	370-390 (br)
1,4-Dimethoxybenzene	0.94	400

^a All electrochemical measurement was performed in CH₂Cl₂ solution (5×10⁻⁴ M) containing 0.1 M *n*-Bu₄NPF₆ at scan rate of 200 mV s⁻¹.

^b All CT bands were measured in CHCl₃.

Table 4

Association constants K_a 's between **1** or **2** and guest molecules in CHCl₃ (298 K)

Entry	Guest compounds	$K_{\rm a}({ m M}^{-1})$	
		1	2
1	1,3,5-Trimethoxybenzene	31.3±2.9 ^a	0.3±0.04
2	1,2,3-Trimethoxybenzene	$1.8 {\pm} 0.02$	<0.1
3	1,2,3,5-Tetramethoxybenzene	$1.6{\pm}0.08$	<0.1

^a The association constant was calculated by nonlinear curve fitting with the 1/1 model using the UV-vis titration data of the charge transfer band, and determined to be $3.1\pm0.29\times10$ M⁻¹ (*R*=0.996).

included between the pyromellitic diimide π -faces in a parallel fashion and the cavity size of the host **1** was ca. 7.0×7.8 Å. In addition, other guest molecules weakly interacted with the imide moiety outside of the cavity (Fig. 10).

The electrostatic potential surfaces (EPSs) predicted that **1** has the electron-deficient surface in the pyromellitic diimide moieties, while the benzene rings of dimethoxybenzenes have the electron-rich surfaces (Fig. 12). The surface of the carbonyl carbon atoms of the diimide moieties is highly electron-deficient, while that of the methoxy oxygen atoms of the guest is electron-rich. The fact that the oxygen atoms of the methoxy groups are located just below the carbonyl carbons of the diimide moieties at two positions in the 1,3-dimethoxybenzene@**1** in the solid state suggested the presence of electrostatic interactions between them, while the overlap is present in only one position in 1,4-dimethoxybenzene@**1** and one complete and one partial overlap were observed in 1,2-dimethoxybenzene@**1** (Fig. 11). Thus the magnitude of the electrostatic interactions was expected to be in the order of 1,3-dimethoxybenzene>1,2-dimethoxybenzene>1,4-dimethoxybenzene.

Furthermore, the crystal data suggested the short contacts between an oxygen atom of the methoxy group and α -hydrogen atoms of the naphthalene ring (d_1 : 2.49 and d_2 : 2.58 Å as well as d_3 : 2.62 and d_4 : 2.57 Å) in 1,3-dimethoxybenzene@**1** (Fig. 13), which are similar to or within the sum of van der Waals radii of oxygen and hydrogen atoms (2.61 Å). Similarly, a pair of C–H···O short (d_1 : 2.61 and d_2 : 2.59 Å) and longer contacts (d_3 : 3.13 and d_4 : 2.87 Å) are present in 1,2-dimethoxybenzene@**1**, while only one pair of C–H···O short contacts exists (d_1 : 2.45 and d_2 : 2.50 Å) in 1,4-dimethoxybenzene@**1**. Bishop et al. proposed the presence of the ether-1,3-*peri* aromatic hydrogen interaction



Figure 10. ORTEP drawing and space filling model of the crystal structures of host-guest complexes between 1 and 1,2-, 1,3- or 1,4-dimethoxybenzene. (a), (d) 1,2-Dimethoxybenzene@1, (b), (e) 1,3-dimethoxybenzene@1, (c), (f) 1,4-dimethoxybenzene@1. Hydrogen atoms and the guest molecules outside of the cavity of 1 are omitted for clarity.

as a stabilizing interaction of oxygenated diquinoline derivatives in the crystal structures, in which the ether oxygen atom interacts with two 1,3-*peri* hydrogens of the quinoline ring of a second molecule with the C-H···O distances being 2.57 and 2.66 Å.¹⁶

The optimum geometry for the ether-1,3-*peri* aromatic hydrogen interaction requires two equal and short C–H···O distances, with the aromatic and ether planes are orthogonal, and with the ether oxygen atom lying in the aromatic plane. In the crystal structures of dimethoxybenzene@1, the naphthalene and ether planes are almost orthogonal (1,3-dimethoxybenzene@1: 87.3 and 85.3°; 1,2-dimethoxybenzene@1: 85.0 and 87.9°; 1,4-dimethoxybenzene@1, 90.0°) and the oxygen atoms are located in the plane of the naphthalene ring (1,3-dimethoxybenzene@1: 0.38 and 1.93 Å; 1,2-dimethoxybenzene@1: 1.83 and 0.33 Å; 1,4-dimethoxybenzene@1, 0.42 Å),

and these data fulfill the requirements of the optimum geometries for the ether-1,3-*peri* aromatic hydrogen interaction. The magnitude of this C–H···O interaction may be decreased in the following order: 1,3dimethoxybenzene>1,2-dimethoxybenzene>1,4-dimethoxybenzenee, and this order is the same as that of the electrostatic interaction. Thus the molecular recognition of dimethoxybenzenes in **1** was ascribed to the combination of the CT, electrostatic, C–H···O, and van der Waals interactions.^{6,17}

Then inclusion behavior between **1** and polymethoxybenzenes with more than three methoxy groups was examined and much



Figure 11. Top views of the crystal structures of the host–guest complexes. The guests outside of the cavity and hydrogen atoms of **1** were omitted for clarity: (a) $1 \cdot 1,2$ -dimethoxybenzene, (b) $1 \cdot 1,3$ -dimethoxybenzene, (c) $1 \cdot 1,4$ -dimethoxybenzene.



Figure 12. Electrostatic potential surfaces: (a) 1 and (b) 1,2-, 1,3-, and 1,4-Dimethoxybenzene and 1,3,5-trimethoxybenzene (B3LYP/6-31G**//B3LYP/6-31G*).







d

smaller K_a values were obtained for 1,2,3-trimethoy- (1.8 M⁻¹) and 1,2,3,5-tetramethoxy-benzene (1.6 M⁻¹) compared to that of 1,3,5trimethoxybenzene (31.3 M^{-1}) (Table 4). The optimized structure (M06/6-31G*)¹⁸ of 1,3,5-trimethox-

ybenzene@1 predicted the similar host-guest overlap to that of 1,3trimethoxybenzene@1, while the naphthalene ring of 1,3,5-trimethoxybenzene@1 was slightly deviated from planarity (Fig. 14). This suggested the presence of the C-H $\cdots\pi$ interactions between the methoxy methyl groups and the naphthalene rings and more suitable C-H···O interactions of the oxygen atom of the methoxy groups and



Figure 14. Optimized structure of 1,3,5-trimethoxybenzene@1' calculated by MO calculation (Gaussian 09, M06/6-31G*,¹⁸ The hexyloxy groups were replaced with methoxy groups in 1.).

Table 5

The oxidation potentials of the guest molecules and the maximum absorption wavelength of the CT bands of the CT complexes between 1 and the guest molecules

Guest compound	$E_{\rm ox}$ (V vs Fc/Fc ⁺) ^a	$\lambda_{CT} (nm)^{b}$
1,3,5-Trimethoxybenzene	1.14	375
1,2,3-Trimethoxybenzene	1.04	370-390 (br)
1,2,3,5-Tetramethoxybenzene	0.68	390-450 (br)

^a All electrochemical measurements were performed in dichloromethane solution (5×10⁻⁴ M) containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate at scan rate of 200 mV s⁻¹. ^b All CT bands were measured in CHCl₃.

α-hydrogen atoms of the naphthalene ring compared to the corresponding interactions expected for 1,3-trimethoxybenzene@1. In addition, van der Waals interactions are expected to be more significant in 1,3,5-trimethoxybenzene@1 than 1,3-dimethoxybenzene@1. The similar oxidation potentials and the wavelengths of the CT bands of



Figure 15. Optimized structures of 1,2,3-trimethoxybenzene by MO calculations (Gaussian03, B3LYP/6-31G*)¹⁹. (a) Top view. (b) Side view. (c) Side view of the crystal structure of the CT complex between 1 and 1,3-dimethoxybenzene. Two pyromellitic diimide moieties and the included 1,3-dimethoxybenzene were presented by the space filling model. 1,3-Dimethoxybenzene outside of the cavity was omitted for clarity.

1,3-dimethoxy- (1.15 V vs Fc/Fc⁺; λ_{max} 370–390 nm) and 1,3,5-trimethoxybenzenes (1.14 V vs Fc/Fc⁺; λ_{max} 375 nm) suggested their similar magnitude of the CT interactions (Table 5). Thus the large K_a value of 1,3,5-trimethoxybenzene@1 may be attributable to the multipoint interactions such as C–H··· π , C–H···O, van der Waals, electrostatic interactions along with CT interactions.

Based on the crystal structures of dimethoxybenzene@**1**, the smaller K_a value of 1,2,3-trimethoxybenzene (1.8 M⁻¹) may be ascribed to the fact that the 1,2,3-trimethoxybenzene cannot take a suitable structure in the cavity of **1**, which enables the CT, electrostatic, and C–H···O interactions effective since the structure, in which all the methoxy groups are located in the same plane of the benzene ring, would be unfavorable due to the steric hindrance of the three consecutive methoxy groups. The B3LYP/6-31G* calculations^{19–23} most optimized the conformation with two coplanar methoxy groups (Fig. 15). Deviation of a methoxy group from the plane of the benzene ring would inhibit insertion of 1,2,3-trimethoxybenzene into the cavity of **1**. Irrespective of the significantly strong electron-donating ability of 1,2,3,5-tetramethoxybenzene, the low K_a value (1.6 M⁻¹) similar to that of 1,2,3-trimethoxybenzene was obtained probably due to similar steric reasons.

3. Conclusions

The *parallel*-conformation of **1** was observed in the crystal structure of dimethoxybenzene@1 and this conformation was expected to be the most stable one by MO calculations. In the electrochemical study, the effective distance of the electronic repulsive interactions between the radical anion and dianion was expected to be ca. 7.3 Å, which is longer than those between the radical anion and neutral species of the imide moieties (ca. 5.0 Å). Although quantitative analysis of the responsible weak molecular interactions is impossible at present, we found that **1** can recognize polymethoxybenzenes by the multipoint interactions such as CT, electrostatic, van der Waals, the C–H···O, and C–H··· π interactions in organic solvent. Thus molecular recognition of polymethoxybenzenes has been accomplished by the neutral host **1** in nonpolar organic solvent, CHCl₃. The synthesis of organic molecular tubes by the stepwise connection of the functionalized host 1 is in progress and the result will be reported elsewhere.

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Supplementary data

General experimental methods, ¹H and ¹³C NMR spectra of **1**, **7**, **8**, and **9**, UV–vis spectra **1** and **1** plus guest molecules, UV–vis spectra **2** and **2** plus guest molecules, ¹H NMR observations of **1** and **2** recorded in CDCl₃ in the presence of guest molecules, structural data for the X-ray analyses, calculated coordinate and total energies of optimized structure of *parallel*-**1**', *syn*-**1**', **9**', 1,2,3-trimethoxybenzene, and 1,3,5-trimethoxybenzene@1', calculated coordinate of 1,2-dimethoxybenzene, 1,3-dimethoxybenzene, 1,4-dimethoxybenzene, and

1,3,5-trimethoxybenzene, and CV traces for guest molecules. CCDC reference number 718293, 718294 and 724380. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.11.087.

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- In the MO calculations, the hexyloxy groups were replaced with methoxy groups in 1, and sum of electronic and zero-point energies were calculated to be -1863381.421 (parallel-1') and -1863379.711 (syn-1') kcal/mol, respectively.
- 10. Even in solution, the *parallel*-conformer of **1** was expected to be a dominant conformer by the comparison of the ¹H NMR spectra of **1** and **9**. The chemical shifts of the proton signals of **1** and **9** are similar except for the inner naph-thalene proton signals H_b, which showed the upfield shift in **1** ($\Delta\delta$ =0.41 ppm) compared to that in **9**. This upfield shift due to the ring current effect of the pyromellitic diimide moieties was ascribed to the preferred *parallel*-conformation of **1**. While the optimized structure of **9** based on MO calculations (Gaussian 03, B3LYP/6-31G⁺) assumes a twisted conformation in which the H_b protons are hardly influenced by the ring current effect of the pyromellitic diimide moieties. In the MO calculations, the hexyloxy groups were replaced with methoxy groups in **9**.
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- 15. The electron-donating ability of the guests was estimated by the oxidation potentials and the wavelengths of the CT bands obtained by the CV measurements and UV-vis spectra, respectively. Based on these data, the electron-donating ability of 1,4-dimethoxybenzene was the strongest in dimethoxybenzenes and 1,2,3- and 1,3,5-trimethoxybenzenes.

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