Self-Assembly of *N,N′*-Bis(2-*tert*-Butylphenyl)pyromellitic Diimide and Phenols or Indoles into a Piled Sandwich Structure. Networks Constructed by Weak Host−Host and Strong Host−Guest Interaction in the Clathrate Compounds

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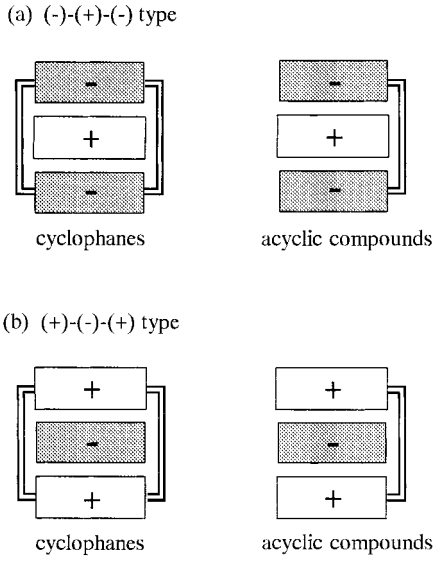
Received June 8, 1999

A novel clathrate host, *N,N′*-bis(2-*tert*-butylphenyl)pyromellitic diimide (**1**), was designed to create a sandwich structure without using cyclophanes nor the acyclic compounds. In the host−guest crystal, the host molecule is sandwiched between two aromatic guest molecules. The inclusion experiment was performed by recrystallization of **1** from chloroform in the presence of the guest at room temperature to give the clathrate compounds. Phenols (phenol, *p*-cresol, α-naphthol, *β*-naphthol, catechol) and indoles (indole, 3-methylindole, 4-methylindole, 5-methylindole) were included in the clathrate compounds, and the host/guest ratio 1:2 was observed in all cases. To explain the mechanism of the self-assembly to the piled sandwich structure, X-ray analysis of the single crystals was performed in all cases. Further, charge-transfer complexation, hydrogen bonding and dipole−dipole interaction were investigated using UV, IR, differential scanning calorimertry (DSC), and AM1 calculation. The order of the decomposition temperature related well with the order of the guest insertion. During the crystallization process, the packing of a guest with a small dipole moment smoothly proceeds and forms a stable clathrate compound. However, a guest which has a large dipole moment generates large electrostatic repulsion in the networks and forms an unstable clathrate compound.

Introduction

In supramolecular chemistry, the inclusion of an aromatic compound between two *π*-conjugated systems using *π*−*π* interactions[1] is one of the most important methods for binding multiple molecules without covalent bonds.[2] These "sandwich" structures can be classified into two types: (1) an electron-poor aromatic compound is held between two electron-rich *π*-conjugated systems (benzenes,[3] naphthalenes,[4] pyrenes,[5] acrydines,[6] and phenanthrenes,[6] Scheme 1a), and (2) holding an electron-rich aromatic compound between two electron-poor *π*-conjugated systems (pyromellitic diimides,[4a,d] 4,4′-dipyridyls,[7] Scheme 1b). In these molecules, the two aromatic systems have to be arranged in parallel at a distance of 6−7 Å.[5] In general, these two aromatic systems are covalently connected to each other by a bridge (diphenylglycolurea,[3] diacetylenes,[4a,b] polyethers,[4c] 1,8-octylene,[4d] steroid,[5] polycyclic aromatics,[6] and *p*-xylylenes[7]). Therefore, the host molecules ought to be either cyclophanes or open rigid acyclic compounds (Scheme 1). Tremendous effort is often needed to synthesize proper host molecules. In this paper, we describe the self-assembly of aromatic

Scheme 1. Sandwich Structures in Supramolecular Chemistry



(1) (a) Cozzi, F.; Cinquini, M.; Annuziata, R.; Siegel, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 5330. (b) Cozzi, F.; Cinquini, M.; Annuziata, R.; Dwyer, T.; Siegel, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 5729. (c) Linse, P. *J. Am. Chem. Soc.* **1993**, *115*, 8793. (d) Linse, P. *J. Am. Chem. Soc.* **1993**, *115*, 4366. (e) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525. (f) Jorgensen, W. L.; Severance, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 4768.

(2) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725.

(3) Reek, J. N.; Priem, A. H.; Engelkamp, H.; Rowan, A. E.; Elemans, J. A. A. W. *J. Am. Chem. Soc.* **1997**, *119*, 9956.

(4) (a) Hamilton, D. G.; Sanders, J. K. M.; Davies, J. E.; Clegg, W.; Teat, S. J. *Chem. Commun.* **1997**, 897. (b) Kennan, A. J.; Whitelock, H. W. *J. Am. Chem. Soc.* **1996**, *118*, 3027. (c) Ortholand, J.-Y.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1394. (d) Jazwinski, J.; Blacker, A. J.; Lehn, J.-M. *Tetrahedron Lett.* **1987**, *28*, 6057.

(5) D′Souza, L. J.; Maitra, U. *J. Org. Chem.* **1996**, *61*, 9494.

(6) Zimmerman, S. C.; Saionz, K. W. *J. Am. Chem. Soc.* **1995**, *117*, 1175.

10.1021/jo990926t CCC: $18.00
Published on Web 09/10/1999

compounds to create a sandwich structure without using cyclophanes or acyclic compounds, as shown in Scheme 1. Our approach is to use a simple aromatic imide as a clathrate host. Crystallization can be used to form clathrates with sandwich structures. No elaborate synthetic procedure is required, in contrast to the aforementioned cyclophanes and acyclic compounds.

Recently, in the field of clathrate chemistry, several examples of host networks constructed by strong intermolecular interactions, such as ionic interaction (sulfonate···guanidinium[8] or carboxylate···ammonium[9]) or strong hydrogen bonding (OH(alcohol)···OH(alcohol),[10] OH(phenol)···OH(phenol),[11] COOH···OH(alcohol),[12] OH(phenol)···N(pyridine),[13] or NH_2···N(triazine)[14]) which include the guest molecules in the cavity of the network, have been reported. Further, besides inclusion compounds, several molecular networks in crystal form due to hydrogen bonding have also been studied.[15] These host networks show high selectivity for specific guest molecules. However, they also have a very narrow range of potential guests because of their rigidity. In contrast, in our method, only weak interactions are used to construct a host network which is flexible enough to adjust for guest inclusion.

We designed *anti*-*N*,*N*′-bis(*tert*-butylphenyl)pyromellitic diimide **1** as a clathrate host with a central aromatic moiety to form a sandwich structure. Two guests (phenols or indoles) would be arranged on either side of the aromatic moiety. Interaction between host and guest molecules was designed to be stronger than that between host molecules. Thus, only weak interaction, such as $\pi-\pi$, CH···π,[16] or CH···O[17] interaction, is used to construct the host network, and strong interaction, such as charge-transfer complexation or hydrogen bonding, is used to strengthen the host−guest network. The weak network of host molecules is expected to offer several advantages: (1) The network is flexible so that its structure can adjust as necessary for the inclusion of guest molecules using host−guest interactions, which makes it more versatile than a rigid network; and (2) The host compound also forms a single crystal in a flexible network. In the case of a strong host network, it is generally difficult to obtain a single crystal of host compound, since empty space in such a crystal cannot be maintained without guest molecules under atmospheric pressure. In contrast, with a flexible host network, it is more likely that the crystal lattice will be able to adjust to give a single crystal.

In general, a crystal of a charge-transfer complex such as a perylene−chloranile complex is known as a D···A structure (1:1, D = donor, A = acceptor) in which the donor and acceptor are alternatively piled up in the crystal.[18] To the best of our knowledge, a guest−host−guest sandwich structure has not yet been reported for the crystal structure of charge-transfer complexes.

Design of the Piled Sandwich Crystal Structure. The piled sandwich structure was designed based on the following strategy (Scheme 2). The interaction by charge transfer must be weak to avoid host−guest 1:1 complexation. For piling up the charge-transferred guest−host−guest complex, some interaction between the sandwich structures is necessary. Thus, network **A** in the *z* direction is constructed using charge-transfer complexation and CH/π interaction. For reinforcement of the network, network **B** in the *x* direction must be constructed using OH/O, NH/O or CH/O, hydrogen bonding between the host and guest, and the host/guest ratio in network **B** must be 1:2. Analysis of this design elucidates the following features that are required for the host and guest: (1) the host must have an electron-poor π-plane at the center of the molecule and the guest is an electron-rich aromatic compound for charge-transfer complexation, (2) the host π-plane must have the same environment on both sides to undergo 1:2 complexation, (3) the host must have two substituents in an *anti*-form to interact with other guest−host−guest complexes for the formation of network **A**, (4) the host must have four hydrogen bond acceptors and the guest must have two hydrogen bond donors to create network **B**, and (5) the host−host interaction in networks **A**′ and **B**′ must be weaker than the host−guest interaction in networks **A** and **B** to construct the piled sandwich structure.

The structure of **1** satisfies all of the requirements for the desired host. The large steric repulsion between *tert*-butyl and the imide-carbonyl oxygens suppresses rotational isomerization around the N−C single bond, and its orthogonal structure is strongly fixed. The two *tert*-butyl groups are locked in an *anti*-form at room temperature. Its four carbonyl groups are available for hydrogen bonding with guests. Electron-rich aromatic compounds which easily generate a charge-transfer complex with **1** are selected as the guests. Inclusion of aromatic com-

(7) (a) Asakawa, M.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Belohradsky, M.; Gandolfi, M. T.; Kocian, O.; Prodi, L.; Raymo, F. M.; Stoddart, J. F.; Venturi, M. *J. Am. Chem. Soc.* **1997**, *119*, 302. (b) Asakawa, M.; Ashton, P. R.; Boyd, S. E.; Brown, C. L.; Gillard, R. E.; Kocian, O.; Raymo, F. M.; Stoddart, J. F.; Tolley, M. S.; White, J. P.; Williams, D. J. *J. Org. Chem.* **1997**, *62*, 26. (c) Devonport, W.; Blower, M. A.; Bryce, M. R.; Goldenberg, L. M. *J. Org. Chem.* **1997**, *62*, 885. (d) Amabilino, D. B.; Dietrich-Buchecker, C. O.; Livoreil, A.; Perez-Garcia, L.; Sauvage, J.-P., Stoddart, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 3905.

(8) Swift, J. A.; Pivovar,, A. M.; Reynolds, A. M.; Ward, M. D. *J. Am. Chem. Soc.* **1998**, *120*, 5887.

(9) (a) Biradha, K.; Dennis, D.; MacKinnon, V. A.; Sharma, C. V. K.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 11894. (b) Sada, K.; Shiomi, N.; Miyata, M. *J. Am. Chem. Soc.* **1998**, *120*, 10543.

(10) (a)Hayashi, N.; Kuruma, K.; Mazaki, Y.; Imakubo, T.; Kobayashi, K. *J. Am. Chem. Soc.* **1998**, *120*, 3799. (b) Udachin, K. A.; Ripmeester, J. A. *J. Am. Chem. Soc.* **1998**, *120*, 1080. (c) Ung, A. T.; Gizachew, U. D.; Bishop, R.; Scudder, M. L.; Dance, I. G.; Craig, D. C. *J. Am. Chem. Soc.* **1995**, *117*, 8745. (d) Hayashi, N.; Mazaki, Y.; Kobayashi, K. *J. Org. Chem.* **1995**, *60*, 6342.

(11) (a) Dewa, T.; Endo, K.; Aoyama, Y. *J. Am. Chem. Soc.* **1998**, *120*, 8933. (b) Endo, K.; Ezuhara, T.; Koyanagi, M.; Masuda, H.; Aoyama, Y. *J. Am. Chem. Soc.* **1997**, *119*, 499. (c) Endo, K.; Koike, T.; Sawaki, T.; Hayashida, O.; Masuda, H.; Aoyama, Y. *J. Am. Chem. Soc.* **1997**, *119*, 4117. (d) Tanaka, K.; Moriyama, A.; Toda, F. *J. Org. Chem.* **1997**, *62*, 1192. (e) Bhyrappa, P.; Wilson, S. R.; Suslick, K. S. *J. Am. Chem. Soc.* **1997**, *119*, 8492. (f) Aoyama, Y.; Endo, K.; Anzai, T.; Yamaguchi, Y.; Sawaki, T.; Kobayashi, K. Kanehisa, N.; Hashimoto, H.; Kai, Y.; Masuda, H. *J. Am. Chem. Soc.* **1996**, *118*, 5562. (g) Endo, K.; Sawaki, T.; Koyanagi, M.; Kobayashi, K.; Masuda, H.; Aoyama, Y. *J. Am. Chem. Soc.* **1995**, *117*, 8341.

(12) Gdaniec, M.; Polonski, T. *J. Am. Chem. Soc.* **1998**, *120*, 7353.

(13) MacGillivray, L. R.; Atwood, J. L. *J. Am. Chem. Soc.* **1997**, *119*, 6931.

(14) (a) Brunet, P.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1997**, *119*, 2737.

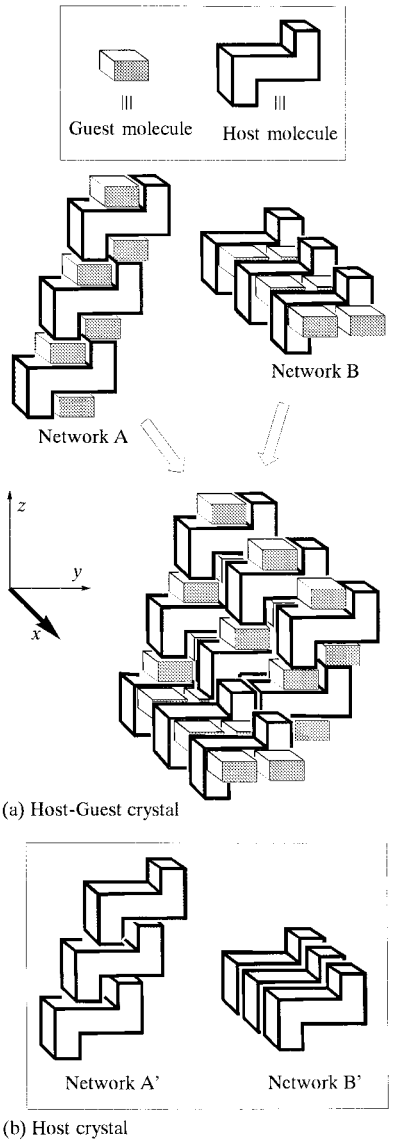
(15) (a) Schauer, C. L.; Matwey, E.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 10245. (b) Coe, S.; Kane, J. J.; Nguyen, T. L.; Toledo, L. M.; Wininger, E.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 86. (c) Lewis, F. D.; Yang, J.-S.; Stern, C. L. *J. Am. Chem. Soc.* **1996**, *118*, 2772. (d) Lewis, F. D.; Yang, J.-S.; Stern, C. L. *J. Am. Chem. Soc.* **1996**, *118*, 12029.

(16) Nishio, M.; Umezawa, Y.; Hirota, M.; Takeuchi, Y. *Tetrahedron* **1995**, *51*, 8665.

(17) (a) Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290. (b) Steiner, T. *Chem. Commun.* **1997**, 727.

(18) (a) Vögtle, F. *Supramolecular Chemistry*; John Wiley & Sons: Chichester, 1991; Chapter 10. (b) Kozawa, K.; Uchida, T. *Acta Crystallogr.* **1983**, *C39*, 1233.

Scheme 2. Design of the Host−Guest ("Piled sandwich structure", (a)) and the Host Crystal Structure (b)



pounds which have no OH or NH group was also investigated to use a hydrogen on an aromatic carbon for CH/O hydrogen bonding with the carbonyl oxygen of **1**. On the basis of the host structure, it is expected that the host will form its own weak two-dimensional network consisting of A′ (CH/π interaction) and B′ (CH/O interaction) without guest molecules (Scheme 2 b).

Synthesis of 1 and Its Clathrate Compounds. An amic acid prepared from pyromellitic anhydride and 2 equiv of 2-*tert*-butylaniline were heated in acetic anhydride at 100 °C to give *N*,*N*′-bis(2-*tert*-butylphenyl)-pyromellitic diimide (Scheme 3). The two stable rotational isomers (*anti*-form (**1**): 40%, *syn*-form (**2**): 41%) were easily separated by conventional column chromatography on silica gel by eluting with chloroform−ethyl acetate. The rotational barrier between the isomers is estimated to be about 28 kcal/mol from our previous report.[19] Recrystallization of **1** from chloroform gives colorless crystals (mp 364 °C). The structure of the *anti*-isomer

(19) Kishikawa, K.; Tsuru, I.; Kohmoto, S.; Yamamoto, M.; Yamada, K. *Chem. Lett.* **1994**, 1605.

Scheme 3. Synthesis of 1 and 2

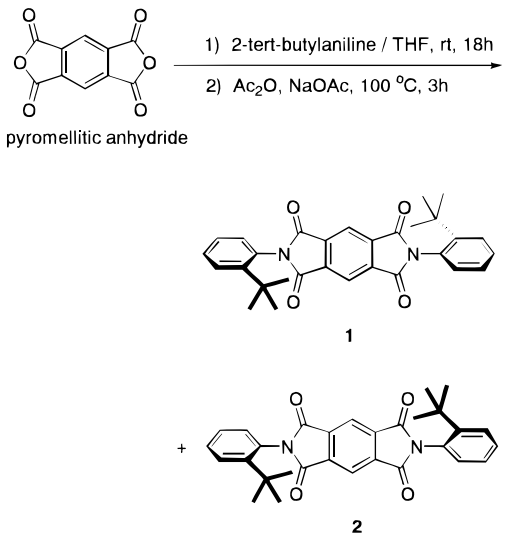


Table 1. Host/Guest Ratio, Color, Habit, and Decomposition Temperature of Clathrate Compounds of 1[a]

entry	guest in clathrate	ratio of host/guest[b]	color, habit	decomposition temperature,[c] °C
1	phenol, **3**	1:2	yellow plates	149.9
2	p-cresol, **4**	1:2	yellow prisms	160.9
3	α-naphthol, **5**	1:2	orange prisms	212.9
4	β-naphthol, **6**	1:2	orange prisms	166.1
5	catechol, **7**	1:2	yellow prisms	153.3
6	indole, **8**	1:2	orange plates	165.2
7	3-methylindole, **9**	1:2	red plates	179.2
8	4-methylindole, **10**	1:2	red plates	186.5
9	5-methylindole, **11**	1:2	orange plates	174.8

[a] Inclusion experiment was performed by recrystallization of **1** from chloroform in the presence of the guests (3 equiv) at room temperature. [b] The host/guest ratio was measured by ^{1}H NMR spectroscopy. [c] Decomposition temperature of the clathrate compounds were measured by a DSC apparatus.

was determined by X-ray crystallography of the single crystal. Only the *anti*-isomer **1** is used as the host molecule in this experiment.

An inclusion experiment was performed by recrystallization of **1** from chloroform in the presence of guests (3 equiv) at room temperature to give yellow, orange, or red crystals, respectively (Table 1). The host/guest ratio was measured by ^{1}H NMR spectroscopy. Phenols (phenol, *p*-cresol, α-naphthol, β-naphthol, catechol) and indoles (indole, 3-methylindole, 4-methylindole, 5-methylindole) were used as clathrate compounds, and a 1:2 ratio was observed in all cases. Other phenols (hydroquinone, resorcinol, phloroglucinol), methylindoles (*N*-, 2-, 6-, and 7-methylindole), and aromatics (benzene, naphthalene, toluene, xylene, aniline, anisole, benzoic acid, benzaldehyde, toluidines) were not included under the same conditions.

X-ray Crystallography of the Clathrate Compounds. The crystal structures of **1** and all of the clathrate compounds were determined by the X-ray analysis of single crystals (Table 2). The pyromellitic diimide π-face of **1** is piled up in parallel in the direction of the *a* axis (Figure 1b). The *tert*-butyl hydrogens contact the aromatic carbons of the pyromellitic diimide of the other host molecule (H5···N3 = 3.13, H5···C6 = 2.81, H5···C7 = 3.07, H5···C9 = 2.95, H5···C12 = 3.34,

Table 2. Crystallographic Data and Packing Coefficients for 1 and Various Adducts

compound	**1**	**1**·(phenol)$_2$	**1**·(*p*-cresol)$_2$	**1**·(α-naphthol)$_2$	**1**·(*β*-naphthol)$_2$	**1**·(catechol)$_2$	**1**·(indole)$_2$	**1**·(3-methylindole)$_2$	**1**·(4-methylindole)$_2$	**1**·(5-methylindole)$_2$
formula	$C_{15}H_{14}NO_2$	$C_{21}H_{20}NO_3$	$C_{44}H_{44}N_2O_6$	$C_{50}H_{44}N_2O_6$	$C_{25}H_{22}NO_3$	$C_{21}H_{20}NO_4$	$C_{23}H_{21}N_2O_2$	$C_{24}H_{23}N_2O_2$	$C_{24}H_{23}N_2O_2$	$C_{24}H_{23}N_2O_2$
rormula weight	240.28	334.39	696.84	768.91	384.46	350.39	357.43	371.46	371.46	371.46
crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic
space group	*P*-1	*P*-1	*P*1	*P*1	*P*-1	*P*21/*c*	*P*21/*c*	*P*-1	*P*-1	*P*-1
Z	2	2	1	1	2	4	4	2	2	2
color	colorless	yellow	yellow	yellow	orange	yellow	orange	red	red	orange
crystal size, mm	0.40 × 0.35 × 0.20	0.40 × 0.15 × 0.15	0.45 × 0.40 × 0.30	0.25 × 0.20 × 0.35	0.25 × 0.20 × 0.35	0.35 × 0.25 × 0.40	0.40 × 0.35 × 0.35	0.25 × 0.25 × 0.10	0.30 × 0.30 × 0.35	0.30 × 0.30 × 0.35
a, Å	8.346(2)[a]	10.22(1)	10.3654(5)	11.278(1)[a]	11.5050(6)	11.876(1)	11.291(1)[a]	10.883(1)	11.354(1)[a]	11.0072(7)
b, Å	10.062(2)	11.89(1)[a]	12.1845(9)[a]	11.879(1)	11.6861(7)[a]	6.010(1)	11.911(1)	11.551(1)[a]	11.5722(9)	11.4941(7)[a]
c, Å	7.867(2)	7.41(1)	7.5077(4)	7.9492(7)	7.7578(4)	25.478(1)[a]	14.2609(9)	8.1722(5)	7.8844(6)	8.1144(6)
α, deg	93.58(2)	91.20(6)	92.503(6)	95.743(8)	96.367(5)			98.996(6)	102.777(6)	94.173(6)
β, deg	106.82(2)	98.65(6)	97.772(4)	97.154(8)	91.121(4)	97.319	94.799(7)	95.241(7)	90.328(8)	93.908(6)
γ, deg	84.89(2)	92.40(1)	93.561(5)	102.080(8)	97.742(5)			100.067(9)	80.439(8)	97.130(5)
V, Å^3	630.8(3)	889.8	926.4(1)	1024.5(2)	1026.5(1)	1803.8(3)	1911.3(3)	991.6(2)	995.7(2)	1012.9(1)
D_{calc}, g/cm^3	1.265	1.248	1.236	1.246	1.244	1.290	1.242	1.244	1.239	1.218
R	0.050	0.086	0.043	0.045	0.068	0.041	0.056	0.062	0.049	0.069
R_W	0.052	0.113	0.049	0.052	0.072	0.035	0.056	0.058	0.050	0.077
GOF	2.13	2.61	2.52	1.88	1.65	1.82	2.50	1.29	2.52	2.81

[a] The molecules are piled up in the direction of the axis.

H9···C6 = 3.35, H9···C7 = 3.26 Å; the sum of the van der Waals radii of H and aromatic C is 2.9−3.1 Å), which indicates the existence of CH/π interaction between the *tert*-butyl hydrogens and the π-face[16] (Figure 1b). Furthermore, the molecules form a network (Figure 1c) in the direction of the *c* axis using CH/O hydrogen bonding of the carbonyl oxygen (O2) with the 3-hydrogen (H15) of the pyromellitic diimide (C12···O2 = 3.36 Å, O2···H15 = 2.51 Å; typical C···O and H···O distances lie in the ranges 3.00−4.00 Å and 2.20−3.00 Å[17]). The CH/π interaction in the direction of the *a* axis and the CH/O hydrogen bonding in the direction of the *c* axis produce the two-dimensional network in the host crystal.

P-1 (phenol, *β*-naphthol, 3-methylindole, 4-methylindole, and 5-methylindole), *P*1 (*p*-cresol and α-naphthol), and *P*21/*c* (catechol and indole) were observed as the space groups (Table 2). Figure 2 shows the crystal structure of clathrate compound **1**·(phenol (**3**))$_2$. Two phenols are set on both faces of the pyromellitic diimide (from the front view (b)) and are slightly apart from the center of the pyromellitic-benzene ring (from the side (c) and top view (d)). The π-plane of the phenols is almost parallel to that of the pyromellitic diimide.

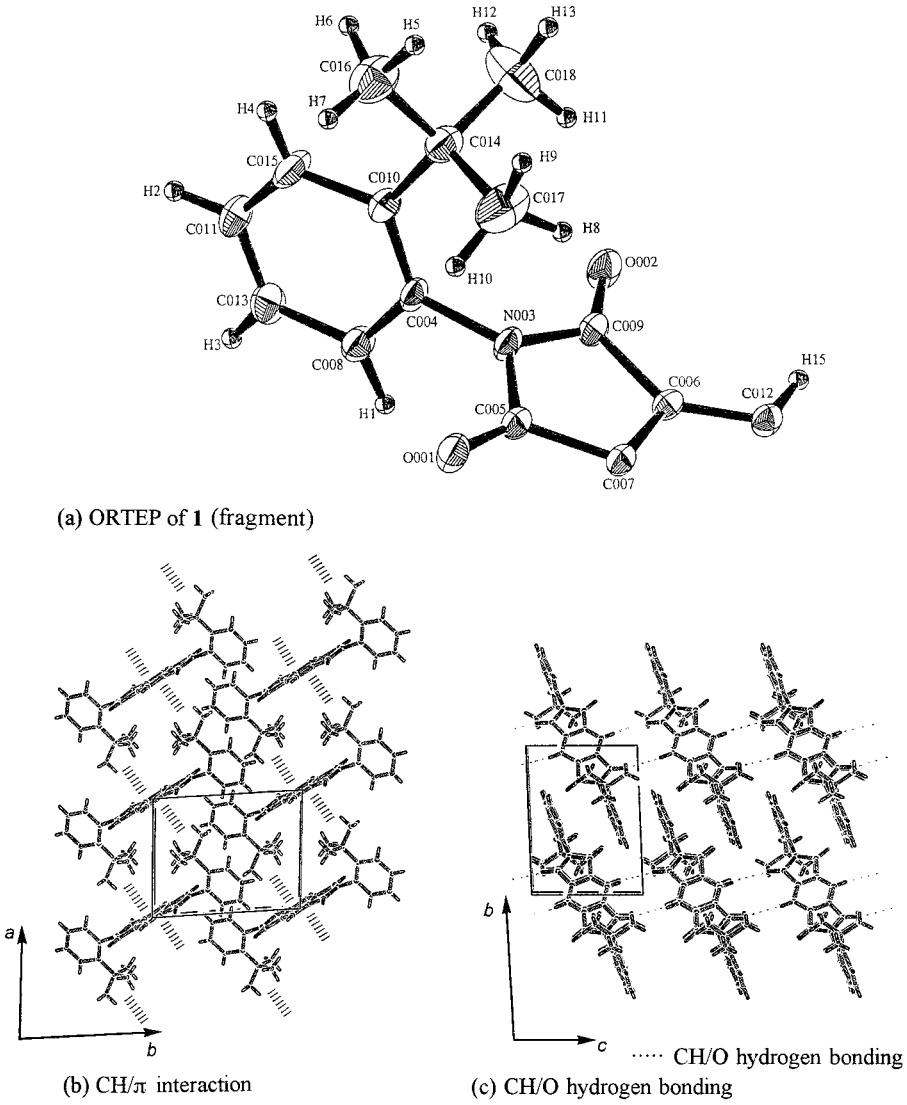
In all cases, two guest molecules and one host assembled to give the piled sandwich structure (Figures 3 and 4). The π-planes of the pyromellitic diimide are piled in parallel in a certain direction (*a* axis for α-naphthol, indole, and 4-methylindole, *b* axis for phenol, *β*-naphthol, *p*-cresol, 3-methylindole, and 5-methylindole, and *c* axis for catechol). The distances between the lattice in the direction of piling increased from 8.36 (host **1**) to 11.01−12.18 Å by insertion of the guest molecules. At the same time, the length of the lattice of the host crystal increased in the range of 2.64 to 4.39 Å. The other two lengths of the lattices changed much less than that in the direction of piling after insertion. In all cases, the π-planes of the guest molecules are also parallel to each other.

The π-plane of the guest is almost parallel to the pyromellitic diimide π-plane of **1** (the angle of these planes is about 10° to 15°) and the guest contacts **1** using $\pi-\pi$ interaction. In clathrate compound **1**·(**3**)$_2$ in Figure 2, the phenol contacts the aromatic carbons of the pyromellitic diimide (O3···C2 = 3.15, C10···C6 = 3.27, C10···C19 = 3.46, C12···O2 = 3.40, C12···C6 = 3.55, C12···C19 = 3.45 Å). The *tert*-butyl hydrogens of **1** contact the aromatic carbon of the guests. In Figure 2, the *tert*-butyl contacts the π-plane of phenol (H11···C13 = 3.09, H11···C17 = 3.20, H17···C10 = 3.02, H17···C13 = 3.18, H17···C17 = 3.07 Å). As a result, the guest molecule is put between the π-plane and the *tert*-butyl group of **1**, and they make network **A** in Scheme 2.

In all cases, network **B** in Scheme 2 was constructed using hydrogen bonding between the host and the guest. Figure 5 shows network **B** of clathrate compound **1**·(4-methylindole (**10**))$_2$. The two carbonyl oxygens of **1** form hydrogen bonding with NH of **10** (O···N = 2.91 Å, O···H = 1.92 Å, O···H−N = 160°) and the other two carbonyls form CH/O hydrogen bonding with the 3-hydrogen of **10** (O···C = 3.44 Å, O···H = 2.57 Å). Network **A** in the direction of piling is reinforced by network **B** in the direction of axis *c* (axis *b* in the case of catechol).

By X-ray crystallography, the piled sandwich structures were ascertained in all cases.

Charge-Transfer Complex of the Host with Phenol or Indole. AM1 calculation[20] (Table 3) indicates the



(a) ORTEP of **1** (fragment)

(b) CH/π interaction

(c) CH/O hydrogen bonding

Figure 1. Crystal structure of **1**.

Table 3. HOMO/LUMO Energy Levels of 1 and Guests[a]

compound	HOMO (eV)	LUMO (eV)
host, **1**	−9.6	−2.1
phenol, **3**	−9.1	0.39
p-cresol, **4**	−8.9	0.43
α-naphthol, **5**	−8.5	−0.37
β-naphthol, **6**	−8.6	−0.35
catecohl, **7**	−9.3	0.18
indole, **8**	−8.4	0.30
3-methylindole, **9**	−8.3	0.31
4-methylindole, **10**	−8.3	0.29
5-methylindole, **11**	−8.4	0.34

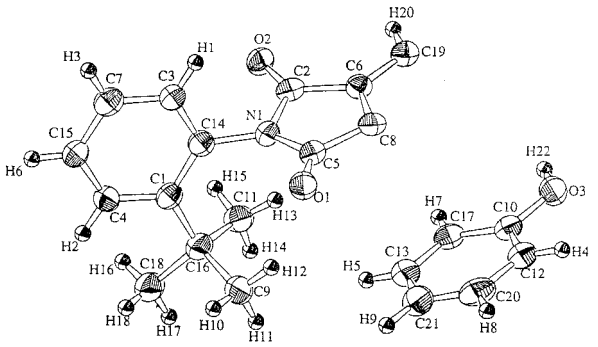
[a]The values were calculated by AM1 method.

possibility of the generation of a charge-transfer complex because the host LUMO (−2.1 eV) is more stable than the LUMOs of the guests (phenol LUMO: 0.4 eV, indole LUMO: 0.3 eV). The energy gap between the host LUMO and phenol HOMO (−7.1 eV) is larger than that between the host LUMO and indole HOMO (−6.4 eV). To investigate the charge-transfer complexation of the host and guest, the UV spectrum of the concentrated solution (host: 1.0×10^{-2} M; guest: 2.0×10^{-2} M in chloroform) was measured. In the case of phenol and indole, charge-transfer bands were observed at 375 and 395 nm, respectively (Charts 1 and 2), and the apparent absorptivity ϵ'_{max} of these absorptions was 3.9. The wavelength of charge-transfer bands (λ_{max}) agrees with those by the calculation.

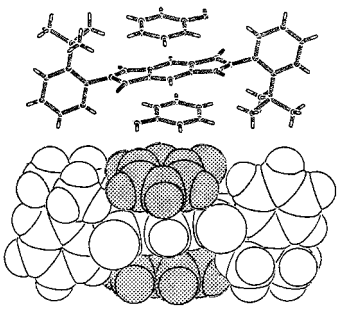
Hydrogen Bonding in the Host and Clathrate Compounds. In IR spectra of crystals of **1**, asymmetric and symmetric stretching vibrations of imide-carbonyl groups were observed at 1776 and 1730 cm^{-1}, respectively. In the crystal structure of **1**, the length between the carbonyl oxygen (O2) and the *β*-hydrogen (H15) was 2.51 Å, which produces a intermolecular CH/O hydrogen bonding by the formation of a ten-membered ring. The oxygen (O1) of the carbonyl also exhibits weak CH/O hydrogen bonding with hydrogens (O1···H1 = 2.83, O1···H3 = 2.71 Å) of the *N*-phenyl group. In the host−guest complexes, the carbonyl absorption at 1730 cm^{-1} moved to 1724−1714 cm^{-1} (Table 4). The strength of the bond was due to hydrogen bonding between the carbonyl oxygen and OH or NH hydrogens of the guests.

In the clathrate compounds, NH or OH stretching vibration of the guests was observed at a lower wavenumber than in the molecules without intermolecular hydrogen bonding in chloroform solution due to hydrogen

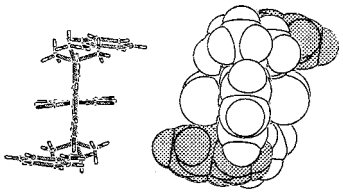
(20) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.



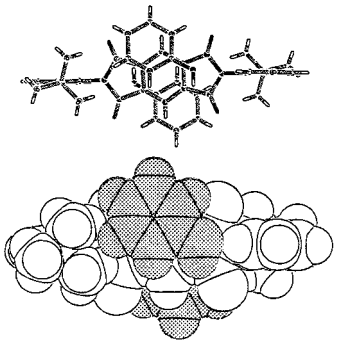
(a) ORTEP of $\mathbf{1}\cdot(\mathbf{3})_2$ (fragment)



(b) front view



(c) side view



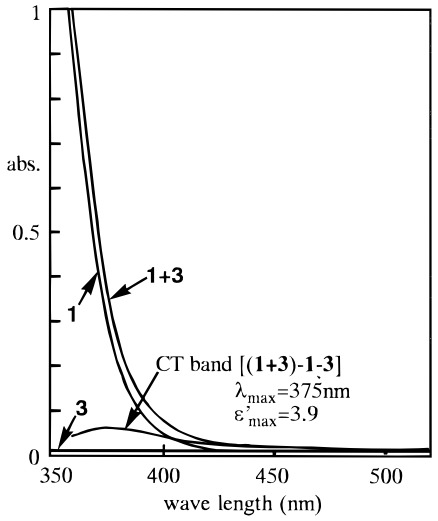
(d) top view

Figure 2. Sandwich structure of $\mathbf{1}\cdot(\mathbf{3})_2$.

bonding with the host carbonyl in the crystal. In chloroform, in the absence of hydrogen bonding, OH peaks of phenols **3**−**7** and NH peaks of indoles **8**−**11** were observed in the range 3604−3560 cm^{-1} and at 3496 cm^{-1}, respectively (Table 5). Peaks of dimerized phenols were seen at 3324−3280 cm^{-1}. In clathrate compounds, the peaks of phenols and indoles were observed at lower ranges: 3516−3440 cm^{-1} and 3460−3380 cm^{-1}, respectively.

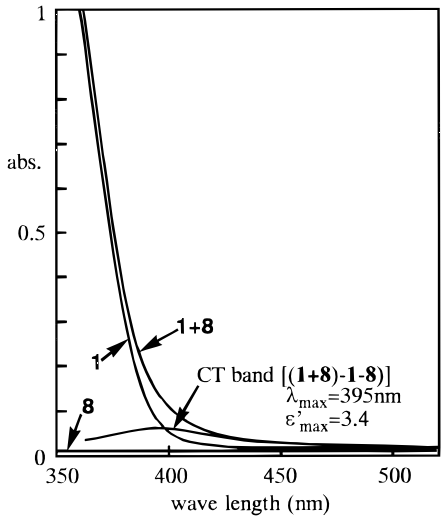
Bond lengths and angles of hydrogen bonds were measured by X-ray crystallography. The distances between the carbonyl oxygen and either the hydroxyl oxygen or the amino nitrogen (O···X, X = O, N) and the angles O···H−X are shown in Table 6. The distances O···X were 2.75−2.89 Å for the clathrates of phenols and 2.86−2.97 Å for those of indoles. The angles of the clathrates of phenols were 157−173° and those of indoles were 143−164°. In general, a shorter distance (D···A) and larger angle (<180°) gave stronger hydrogen bonding. Some of the hydrogen-bonded C═O showed a longer

Chart 1. UV Spectra of 1, 3, 1 + 3 (1:3 = 1:2) and the Charge Transfer (CT) Band in $CHCl_3$[a]



[a] [**1**] = 1.0 × 10^{-2} M, [**3**] = 2.0 × 10^{-2} M, [**1**+**3**] = ([**1**] = 1.0 × 10^{-2} M). UV data of **1**: $\lambda_{max}(\epsilon)$ 243.5 nm (31000), 246.5 nm (s), 307.5 (2850), 318 nm (3050).

Chart 2. UV Spectra of 1, 8, 1 + 8 (1:8 = 1:2) and the Charge Transfer (CT) Band in $CHCl_3$[a]



[a] [**1**] = 1.0 × 10^{-2} M, [**8**] = 2.0 × 10^{-2} M, [**1**+**8**] = ([**1**] = 1.0 × 10^{-2} M), **8** = 2.0 × 10^{-2} M).

Table 4. IR Peaks of the Carbonyls in the Host Crystal and the Clathrate Compounds[a]

	ν (cm^{-1})	
crystal	C═O(1)	C═O(2)
host, **1**	1776	1730
host·phenol, $\mathbf{1}\cdot(\mathbf{3})_2$	1776	1720
host·*p*-cresol, $\mathbf{1}\cdot(\mathbf{4})_2$	1776	1716
host·α-naphthol, $\mathbf{1}\cdot(\mathbf{5})_2$	1774	1722
host·*β*-naphthol, $\mathbf{1}\cdot(\mathbf{6})_2$	1774	1714
host·catecohl, $\mathbf{1}\cdot(\mathbf{7})_2$	1774	1722
host·indole, $\mathbf{1}\cdot(\mathbf{8})_2$	1774	1722
host·3-methylindole, $\mathbf{1}\cdot(\mathbf{9})_2$	1768	1718
host·4-methylindole, $\mathbf{1}\cdot(\mathbf{10})_2$	1772	1724
host·5-methylindole, $\mathbf{1}\cdot(\mathbf{11})_2$	1772	1718

[a] The IR spectra were measured by KBr method.

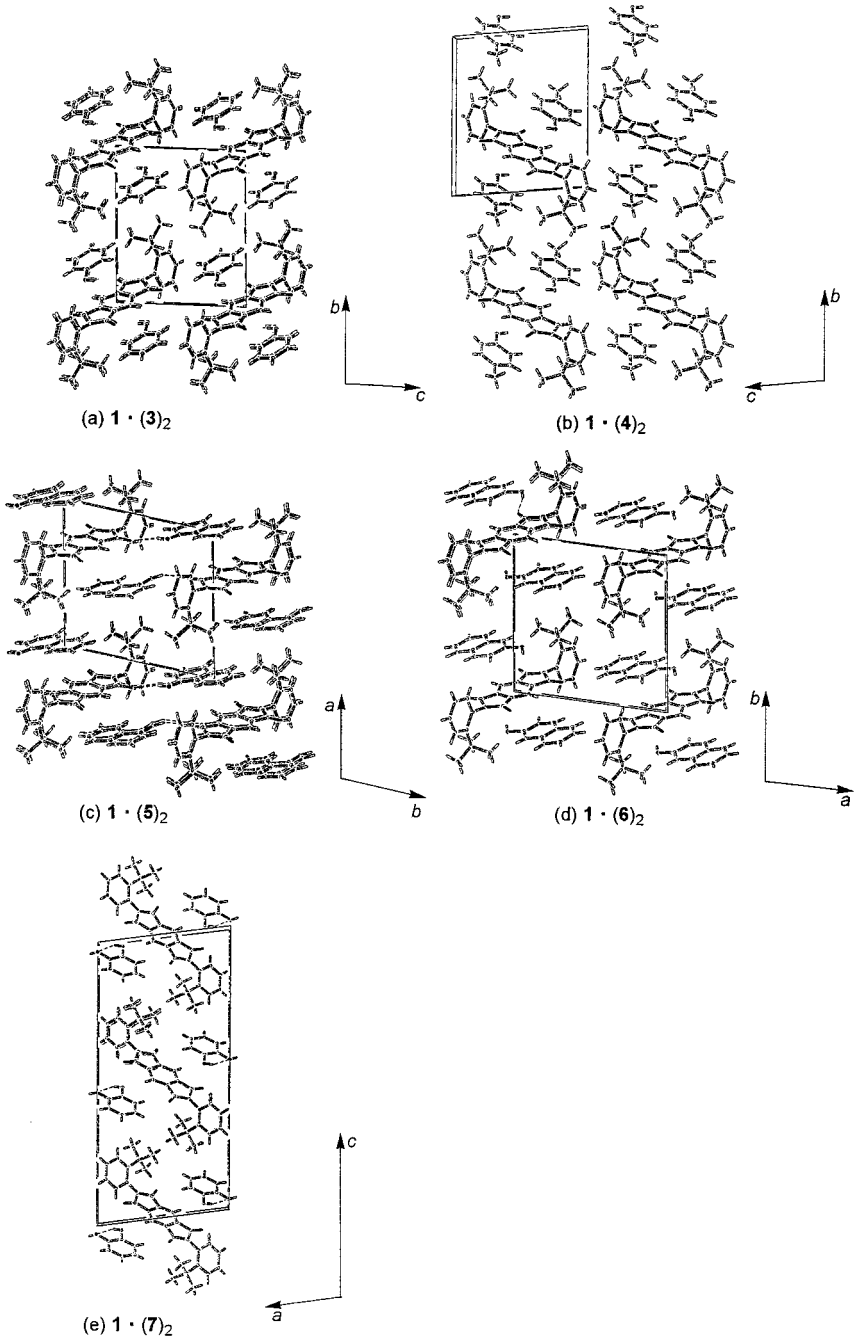


Figure 3. Crystal structure of clathrate compounds of **1** and phenols.

Table 5. OH and NH Peaks in IR Spectra of the Guests

	ν (cm^{-1})	
guest	in $CHCl_3$ solution[a]	in clathrate compound[b]
phenol, **3**	3600, 3308	3440
p-cresol, **4**	3600, 3324	3468, 3424
α-naphthol, **5**	3600, 3324	3468
β-naphthol, **6**	3600, 3316	3468
catecohl, **7**	3560, 3280	3516, 3440
indole, **8**	3496	3380
3-indole, **9**	3496	3460
4-indole, **10**	3496	3404
5-indole, **11**	3496	3396

[a] IR spectrum concentration of chloroform solution was adjusted to 50 mM. [b] The IR spectra were measured by KBr method.

distance than non-hydrogen-bonded C=O. In this series, it is clear that clathrates of phenols have stronger hydrogen bonds than indoles. These bond distances, 2.75−2.89 Å for phenols and 2.86−2.97 Å for indoles, are typical of hydrogen bonds.[21]

Order of the Ability of Guests To Be Inserted into Clathrate Compounds. In this series of guests, the order of insertion ability was determined by competitive cocrystallization with **1**. The host (10 mg) and two kinds of guests (guest A: 3 equiv, guest B: 3 equiv) were dissolved in chloroform (1 mL), and the solution was slowly concentrated under atmospheric conditions to give the clathrate compounds. Table 7 shows the ratios of the resulting clathrate compounds, and the ratios of (guest A)/host, (guest B)/host, and (guest A)/(guest B). The order of the ability to be inserted was determined based on this information. The most strongly included guest is **5**, while

(21) Nakamoto, K.; Margoshes, M.; Rundle, R. E. *J. Am. Chem. Soc.* **1955**, *77*, 6480.

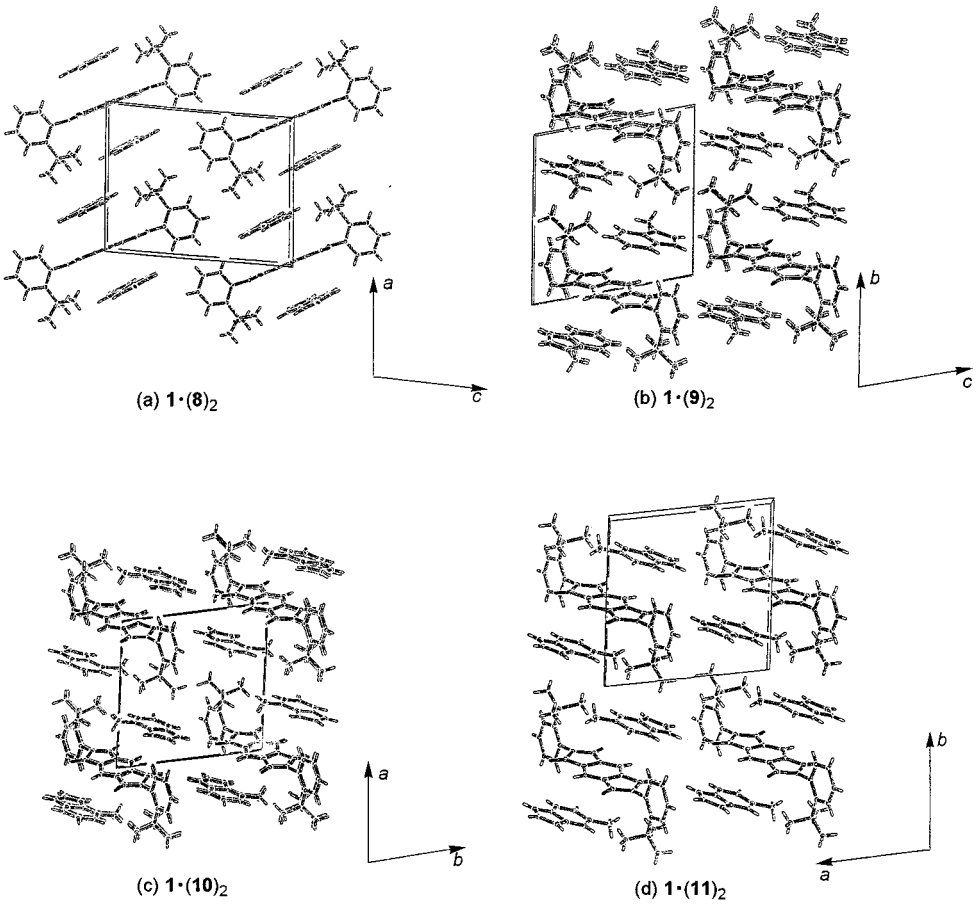


Figure 4. Crystal structure of clathrate compounds of **1** and indoles.

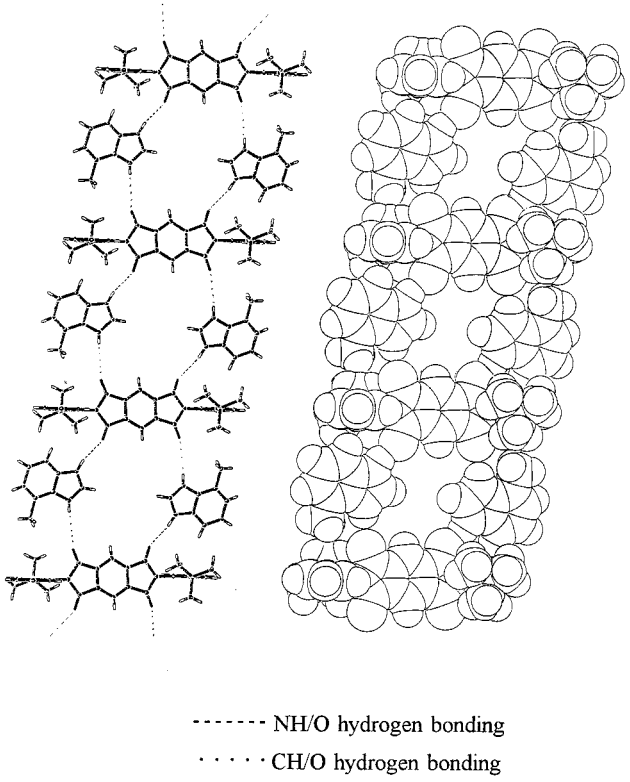
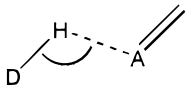


Figure 5. Hydrogen bond network of **1**·(**10**)$_2$.

10 is second in this order (Scheme 4). Guests **6**, **8**, **9**, and **11** show almost equivalent ability. Guests **4** and **6** are included similarly, but with lower inclusion ability than **8**, **9**, and **11**. The most weakly included guest is **7** and then **3**.

Table 6. Lengths and Angles of Hydrogen Bonds in the Clathrate Compounds



(D = O or N. A = O)

entry	crystal	length (Å) of D···A	length (Å) of D−H	length (Å) of H···A	angle (deg) of D−H···A	length (Å) of the host carbonyls: hydrogen-bonded	length (Å) of the host carbonyls: no hydrogen-bonded
1	**1**	-	-	-	-	(1.20)	(1.19)
2	**1**·(3)$_2$	2.75	0.95	1.83	163	1.21	1.21
3	**1**·(4)$_2$	2.76	1.03	1.73	173	1.25	1.20
		2.75	0.88	1.91	160	1.16	1.20
4	**1**·(5)$_2$	2.79	0.94	1.90	159	1.20	1.19
		2.75	0.99	1.81	157	1.21	1.21
5	**1**·(6)$_2$	2.89	1.04	1.90	158	1.21	1.20
6	**1**·(7)$_2$	2.79	0.83	1.98	165	1.21	1.20
7	**1**·(8)$_2$	2.86	0.95	2.02	147	1.20	1.20
8	**1**·(9)$_2$	2.97	0.95	2.15	143	1.20	1.20
9	**1**·(10)$_2$	2.91	1.02	1.92	160	1.20	1.20
10	**1**·(11)$_2$	2.97	0.94	2.05	164	1.20	1.18

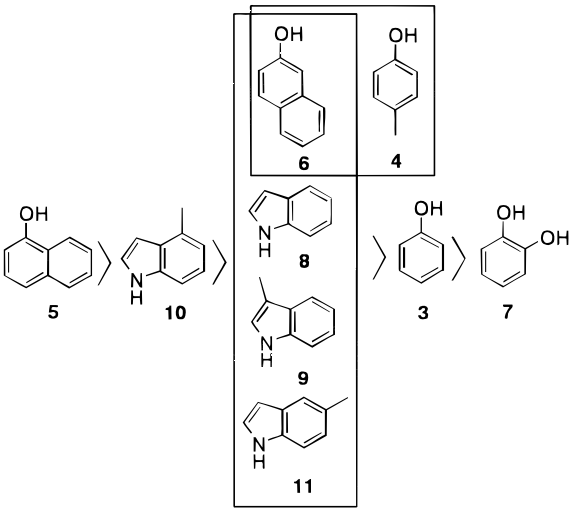
The insertion of phenol (**3**) into host crystals and exchange of the guests from phenol (**3**) to indole (**8**) were observed by a powder X-ray diffraction analysis. After grinding host crystals with **3** for 1 min, the diffraction pattern of crystal **1** disappeared and that of clathrate compound **1**·(**3**)$_2$ appeared. This indicated that **3** had been inserted in the crystal lattice of **1**. Moreover, exchange

Table 7. Competitive Cocrystallization of Host 1[a]

entry	guest A	guest B	A/**1**	B/**1**	(A+B)/**1**	A/B	entry	guest A	guest B	A/**1**	B/**1**	(A+B)/**1**	A/B
1	**3**	**4**	0.7	1.3	2.0	0.5	19	**5**	**9**	1.7	0.3	2.0	5.7
2	**3**	**5**	0.0	2.0	2.0	0.0	20	**5**	**10**	1.9	0.1	2.0	19.0
3	**3**	**6**	0.0	2.0	2.0	0.0	21	**5**	**11**	1.8	0.2	2.0	9.0
4	**3**	**7**	1.1	0.9	2.0	1.2	22	**6**	**7**	1.2	0.8	2.0	1.5
5	**3**	**8**	0.3	1.7	2.0	0.4	23	**6**	**8**	1.0	1.0	2.0	1.0
6	**3**	**9**	0.0	2.0	2.0	0.0	24	**6**	**9**	1.0	1.0	2.0	1.0
7	**3**	**10**	0.0	2.0	2.0	0.0	25	**6**	**10**	1.0	1.0	2.0	1.0
8	**3**	**11**	0.0	2.0	2.0	0.0	26	**6**	**11**	1.0	1.0	2.0	1.0
9	**4**	**5**	0.0	2.0	2.0	0.0	27	**7**	**8**	0.5	1.5	2.0	1.0
10	**4**	**6**	1.0	1.0	2.0	1.0	28	**7**	**9**	0.1	1.9	2.0	0.05
11	**4**	**7**	1.7	0.3	2.0	5.7	29	**7**	**10**	0.0	2.0	2.0	0.0
12	**4**	**8**	0.8	1.2	2.0	0.7	30	**7**	**11**	0.0	2.0	2.0	0.0
13	**4**	**9**	0.4	1.6	2.0	0.3	31	**8**	**9**	1.0	1.0	2.0	1.0
14	**4**	**10**	1.3	0.7	2.0	1.9	32	**8**	**10**	0.4	1.6	2.0	0.3
15	**4**	**11**	1.4	0.6	2.0	2.3	33	**8**	**11**	1.0	1.0	2.0	1.0
16	**5**	**6**	2.0	0.0	2.0	vl[b]	34	**9**	**10**	0.9	1.1	2.0	1.0
17	**5**	**7**	2.0	0.0	2.0	vl[b]	35	**9**	**11**	1.0	1.0	2.0	1.0
18	**5**	**8**	2.0	0.0	2.0	vl[b]	36	**10**	**11**	1.6	0.4	2.0	4.0

[a] The host **1** (10 mg) and two kinds of guests (guest A: 3 equiv, guest B: 3 equiv) were dissolved in chloroform (1 mL), and the solution was slowly concentrated under the atmospheric condition to afford the clathrate compounds. The ratios of obtained clathrate compounds and the ratio of (guest A)/host, (guest B)/host, and (guest A)/(guest B) were determined by ^{1}H NMR. [b] Very large.

Scheme 4. Order of Guest Insertion in Crystallization from $CHCl_3$



of the guests was investigated. After mixing crystal **1**·(**3**)$_2$ with **8**, the peaks of clathrate **1**·(**3**)$_2$ disappeared and those of clathrate **1**·(**8**)$_2$ were observed. This means that **3** had been replaced with **8** in the clathrate compound. Accordingly, the crystal structure of **1** is flexible for the insertion and exchange of guests. The order of inclusion ability, (guest A)/(guest B), reflects the equilibrium ratios of the guests in the solid phase (Table 7).

DSC Experiments with 1 and the Clathrate Compounds. The decomposition temperatures (dp) of the clathrate compounds were measured by a DSC apparatus (Table 1). Clathrate **1**·(**5**)$_2$ gave the highest dp (212.9 °C) in this series, followed by **1**·(**10**)$_2$ (186.5 °C). The lowest dp was seen for **1**·(**3**)$_2$ (149.9 °C), which was immediately below that for **1**·(**7**)$_2$ (153.3 °C). The order of the dp closely agreed with the order of guest insertion. The dp may be controlled by the total amount of stabilization energy for the formation of the clathrate compound. The total stabilization energy consists of hydrogen bonding, charge-transfer complexation, dipole−dipole interaction, and so on. After decomposition, all of the compounds showed a sharp peak of **1** corresponding to its melting point 359.0−363.5 °C. Incidentally, the pure host crystal showed an exothermic heat of 17.2 cal/g at 364.0 °C, which meant that crystallized **1** was 8.3 kcal/mol more stable than the liquid host at this temperature. This indicates that the host network is restructured after decomposition of the clathrate compound followed by release of the guest molecules. The DSC experiment of **1**·(**5**)$_2$ showed −25.9 cal/g during decomposition. This indicates that 1 mol of crystallized host(α-naphthol)$_2$ is 20 kcal/mol more stable than a mixture of the solid host (1 mol) and liquid α-naphthol (2 mol) at 212.9 °C. The value 20 kcal/mol is thought to be the total amount of stabilization energy for the formation of **1**·(**5**)$_2$.

Crystal Structure and Dipole−Dipole Interaction. The direction and value of dipole moments were calculated by the AM1 method.[9] These values, along with the relative host−guest arrangements in the crystal structure, are illustrated in Figure 6. In the case of phenols **3**−**7**, the guest O−H bond and the host C═O are arranged in a parallel direction. The direction of the dipole of **6** is the only one different from the other phenols. In the case of indoles **8**−**11**, the directions of their dipole moments are also very similar. The smallest calculated dipole moment is 0.90 D for **5**, while the largest one is 2.13 D for **7**. Although **1** has no dipole moment because of its symmetric structure, each imide-carbonyl generates partially polarized areas on the molecule. The guest O−H or N−H bond and the host C═O are arranged in parallel at a short distance, and the dipole moments of the guests are canceled by the C═O dipole moment of **1**. The dipole−dipole interaction between the host and guest may greatly influence the host−guest arrangement in crystal structures, as observed in these X-ray structures.

Mechanism of the Self-Assembly of the Host and Guests into a Piled Sandwich Structure. The host crystal structure is only constructed by two kinds of weak networks. One is made by CH/π interaction between *tert*-butyl hydrogens and pyromellitic benzene rings, and the other is made by CH/O hydrogen bonding between hydrogen of the pyromellitic benzene ring and a carbonyl oxygen. In contrast, the crystal structure of the host−guest complex is constructed by strong interactions: hydrogen bonding and charge-transfer complexation. Interaction between the host and guest is stronger than

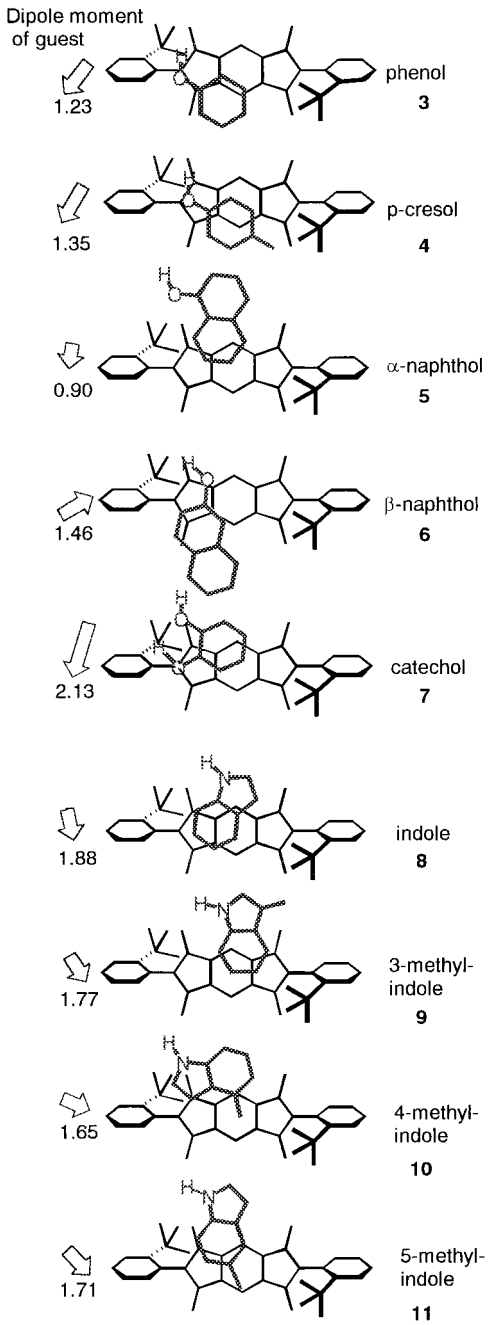


Figure 6. Dipole moments (debye) of the guests and structure of the clathrate compounds (top view).

that between the hosts. This is why the host crystals include the guest molecules to make a host−guest network.

The mechanism of the assembly into the piled sandwich structure is postulated to be as follows. The *tert*-butyl groups on the *N*-phenyl groups of **1** make a suitable space for the guest (about 3.5 Å) on both sides of the pyromellitic plane. The symmetrical structure of **1** and weak charge-transfer complexation with the guests allow for the unique host−guest ratio of 1:2, although charge-transfer complexes are usually crystallized in a ratio of 1:1. Furthermore, each of the two carbonyls of **1** is used to bind a guest by hydrogen bonding, while two other carbonyls are used to cancel the dipole moment of the guest and for CH/O hydrogen bonding with the guest.

Compound **5** has the smallest dipole moment, while **7** has the largest dipole moment. On the basis of the present results, the dipole moment greatly influences the order of the ability of insertion. During crystallization of these clathrate compounds, the following three interactions between the host and guest are important: (1) hydrogen bonding between the host carbonyl oxygen and the hydrogen on the heteroatom of the guest, (2) charge-transfer complexation of the host and the guest, and (3) dipole−dipole interaction between the host carbonyl group and the guest molecule. The association constant (K_a) of **1** with phenol was too small (K_a <1) to measure in a titration experiment using ^{1}H NMR spectroscopy in chloroform. Hydrogen bonding and charge-transfer complexation are effective at locating the host and guest at a short separation. Hydrogen bonding produces the network **B**, while the other network (**A**) is the result of charge-transfer complexation and CH/π interaction. In this process, if the energy level of the guest's HOMO is low, charge transfer only has a small effect. The low HOMO energy levels of **7** and **3** (−9.3 and −9.1 kcal/mol) might explain their low insertion ability. At a short intermolecular distance, dipole−dipole interaction controls the packing structure, resulting in the cancelation of electrostatic repulsion between the host and guest. In this process, the insertion of a guest with a small dipole moment proceeds smoothly to forms a stable clathrate compound. However, a guest with a large dipole moment generates large electrostatic repulsion in the networks and forms an unstable clathrate compound.

Conclusion

In this study, we confirmed that it is possible to assemble three aromatic compounds into a "sandwich" structure without using conventional techniques, such as the usage of cyclophanes or acyclic compounds, and without any tedious synthesis to join the two aromatic moieties.

The following results were obtained: (1) The network constructed by weak host−host interactions is flexible for guest inclusion. Single crystals of both host and host−guest can be obtained to give much information on the inclusion by X-ray crystallography. In this series, similar crystal structures were observed for all of the inclusion compounds regardless of the volume of the guest molecule, although each inclusion compound has its own lattice parameters in the crystal. (2) Strong host−guest interactions, i.e., hydrogen bonding and charge-transfer complexation, are the main driving force to produce the sandwich-type supramolecular structure. (3) With broad selectivity, the host network can include aromatic compounds, which have a proton for hydrogen bonding and an HOMO energy level of −9.1 to −8.3 eV. (4) In this system, the order of the ability to be inserted can be estimated from the dipole moment of the guest molecule and the transfer energy of the host−guest crystal by DSC.

Using several weak interactions in a crystal, an architecture which cannot be assembled in solution can be synthesized as a clathrate compound. The construction of a sandwich structure using simple aromatic compounds based on our idea simplifies the synthesis of supramolecules.

Experimental Section

General. In measurement of IR spectrum concentration of chloroform solution was adjusted to 25 mM in the case of **1** and 50 mM in the case of the guest. UV spectra were measured

in 1.0×10^{-5} M solution of **1** and 2.0×10^{-5} M solution chloroform of the guest. The single crystals of the clathrate compounds were obtained by recrystallization from chloroform at room temperature. The X-ray crystal diffraction was measured by Rigaku AFC7S and Raxis. The measurement was performed at 100 K (in the case of host−phenol complex) and 296 K (in other cases). Structure solution was carried out by direct methods (SIR 92) and refinement by full-matrix least-squares.

Synthesis of *N,N′*-Bis(2-*tert*-butylphenyl)pyromellitic Diimide. Pyromellitic anhydride (2.00 g, 9.17 mmol) was suspended in THF (30 mL). A solution of 2-*tert*-butylaniline (2.86 mL, 18.34 mmol) in THF (10 mL) was added dropwise within 12 min, and the reaction mixture was stirred at room temperature for 18 h. The white solid was obtained by filtration with suction and dried in vacuo to give the amic acid (4.71 g, 99%).

The amic acid (4.69 g, 9.08 mmol), sodium acetate (0.75 g, 9.08 mmol), and acetic anhydride (60 mL) were heated at 100 °C for 3 h. After cooling to room temperature, the excess acetic anhydride and generated acetic acid were evaporated. Chloroform (50 mL) and water (50 mL) were added to the solid, and the solution was stirred for 10 min. The chloroform extract was washed with saturated aqueous $NaHCO_3$ solution (three 50 mL portions), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The *anti*- and *syn*-isomers were separated by column chromatography on silica gel eluting with chloroform−ethyl acetate. The obtained isomers were recrystallized from *n*-hexane-chloroform to give *anti*-isomer (1.78 g, 41%) and *syn*-isomer (1.76 g, 40%).

***anti-N,N′*-Bis(2-*tert*-butylphenyl)pyromellitic diimide (1):** mp 364.0 °C, colorless plates; IR (KBr) 3076 (aromatic C−H), 2968 (aliphatic C−H), 1776 (C═O), 1730 (C═O), 1494, 1440, 1376 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.32 (s, 18H), 7.00 (dd, J = 7.8, 1.5, 2H), 7.35 (td, J = 7.3, 1.5, 2H), 7.48 (td, J = 8.1, 1.5, 2H), 7.67 (dd, J = 8.1, 1.5, 2H), 8.52 (s, 2H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 17.72 (q), 126.74 (d), 128.89 (d), 129.27 (s), 129.93 (s), 131.00 (d), 134.22 (d), 136.40 (s), 169.46 (s); UV λ_{max} (ϵ) 243.5 (31000), 246.5 (s), 307.5 (2850), 318 nm (3050). Anal. Calcd for $C_{11}H_9NO_2$: C, 70.58; H, 4.85; N, 7.48. Observed: C, 70.57; H, 4.64; N, 7.47.

***syn-N,N′*-Bis(2-*tert*-butylphenyl)pyromellitic diimide (2):** mp 362.9 °C, colorless needles; IR (KBr) 3080 (aromatic C−H), 2972 (aliphatic C−H), 1778 (C═O), 1724 (C═O), 1496, 1442, 1382 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.34 (s, 18H), 7.03 (dd, J = 7.8,1.5, 2H), 7.35 (td, J = 7.8, 1.5, 2H), 7.48 (td, J = 8.1, 1.5, 2H), 7.67 (dd, J = 8.1, 1.5, 2H), 8.50 (s, 2H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 17.72 (q), 126.74 (d), 128.89 (d), 129.27 (s), 129.93 (s), 131.00 (d), 134.22 (d), 136.40 (s), 169.46 (s). Anal. Calcd for $C_{11}H_9NO_2$: C, 70.58; H, 4.85; N, 7.48. Observed: C, 70.57; H, 4.64; N, 7.47.

Host(phenol)$_2$ complex 1·(3)$_2$: dp 149.9 °C, yellow plates; IR (KBr) 3440 (O−H), 3044 (aromatic C−H), 2964 (aliphatic C−H), 1776 (C═O), 1720 (C═O), 1594, 1500, 1476, 1442, 1378 cm^{-1}; IR ($CHCl_3$) 3600 (O−H), 3308 (O−H), 3032 (aromatic C−H), 2968 (aliphatic C−H), 1776 (C═O), 1728 (C═O), 1598, 1500, 1472, 1444, 1378 cm^{-1}; UV λ_{max} (ϵ) 244 (27500), 247 (s), 267 (s), 275 (s), 308 (2400), 318 nm (2600).

Host(*p*-cresol)$_2$ complex 1·(4)$_2$: dp 160.9 °C, yellow prism; IR (KBr) 3468 (O−H), 3424 (O−H), 3076 (aromatic C−H), 2992 (aliphatic C−H), 1776 (C═O), 1716 (C═O), 1514, 1444, 1378 cm^{-1}; IR ($CHCl_3$) 3600 (O−H), 3324 (O−H), 2968 (aliphatic C−H), 1776 (C═O), 1728 (C═O), 1598, 1512, 1494, 1444, 1378 cm^{-1}.

Host(α-naphthol)$_2$ complex 1·(5)$_2$: dp 212.9 °C, orange blocks; IR (KBr) 3468 (O−H), 2964 (aliphatic C−H), 1774 (C═O), 1722 (C═O), 1580, 1490, 1460, 1444, 1380 cm^{-1}; IR ($CHCl_3$) 3600 (O−H), 3324 (O−H), 2968 (aliphatic C−H), 1778 (C═O), 1728 (C═O), 1598, 1580, 1494, 1444, 1378 cm^{-1}.

Host(β-naphthol)$_2$ complex 1·(6)$_2$: dp 166.1 °C, orange blocks; IR (KBr) 3468 (O−H), 3056 (aromatic C−H), 2968 (aliphatic C−H), 1774 (C═O), 1714 (C═O), 1638, 1514, 1446, 1386 cm^{-1}; IR ($CHCl_3$) 3600 (O−H), 3316 (O−H), 3024 (aromatic C−H), 2968 (aliphatic C−H), 1778 (C═O), 1728 (C═O), 1632, 1604, 1494, 1444, 1378 cm^{-1}.

Host(catechol)$_2$ complex 1·(7)$_2$: dp 153.3 °C, yellow columns; IR (KBr) 3516 (O−H), 3440 (O−H), 3072 (aromatic C−H), 2964 (aliphatic C−H), 1774 (C═O), 1722 (C═O), 1616, 1514, 1492, 1470, 1448, 1384 cm^{-1}; IR ($CHCl_3$) 3604 (O−H), 3560 (O−H), 3280 (O−H), 3024 (aromatic C−H), 2972 (aliphatic C−H), 1776 (C═O), 1728 (C═O), 1608, 1512, 1494, 1472, 1444, 1376 cm^{-1}.

Host(indole)$_2$ complex 1·(8)$_2$: dp 165.2 °C, orange plates; IR (KBr) 3380 (N−H), 2964 (aliphatic C−H), 1774 (C═O), 1722 (C═O), 1492, 1442, 1378, 1364 cm^{-1}; IR ($CHCl_3$) 3496 (N−H), 2968 (aliphatic C−H), 1778 (C═O), 1728 (C═O), 1494, 1444, 1376 cm^{-1}; UV λ_{max} (ϵ) 245 (32000), 247.5 (s), 267 (s), 277 (s), 287.5 (8300), 308.5 (2200), 319 nm (2450).

Host(3-methylindole)$_2$ complex 1·(9)$_2$: dp 179.2 °C, red plates; IR (KBr) 3460 (N−H), 3036 (aromatic C−H), 2964 (aliphatic C−H), 1768 (C═O), 1718 (C═O), 1620, 1492, 1442, 1368 cm^{-1}; IR ($CHCl_3$) 3496 (N−H), 2972 (aliphatic C−H), 1778 (C═O), 1728 (C═O), 1494, 1444, 1376 cm^{-1}.

Host(4-methylindole)$_2$ complex 1·(10)$_2$: dp 186.5 °C, red plates; IR (KBr) 3404 (N−H), 3060 (aromatic C−H), 2964 (aliphatic C−H), 1772 (C═O), 1724 (C═O), 1494, 1446, 1380, 1368 cm^{-1}; IR ($CHCl_3$) 3496 (N−H), 3004 (aromatic C−H), 2972 (aliphatic C−H), 1778 (C═O), 1728 (C═O), 1494, 1444, 1378 cm^{-1}.

Host(5-methylindole)$_2$ complex 1·(11)$_2$: dp 174.8 °C, orange plates; IR (KBr) 3396 (N−H), 3084 (aromatic C−H), 2960 (aliphatic C−H), 1772(C═O), 1718(C═O), 1628, 1580, 1492, 1442, 1368 cm^{-1}; IR ($CHCl_3$) 3496 (N−H), 2972 (aliphatic C−H), 1778 (C═O), 1728 (C═O), 1494, 1444, 1376, 1320 cm^{-1}.

Supporting Information Available: X-ray crystallographic data (tables of atomic coordinates, thermal parameters, bond lengths, bond angles, and torsion angles and ORTEP diagrams) for **1**, **1·(3)$_2$**, **1·(4)$_2$**, **1·(5)$_2$**, **1·(6)$_2$**, **1·(7)$_2$**, **1·(8)$_2$**, **1·(9)$_2$**, **1·(10)$_2$**, and **1·(11)$_2$**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO990926T