A Versatile Tripodal Host with Cylindrical Conformation: Solvatomorphism, Inclusion Behavior, and Separation of Guests

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Abstract: Tripodal host 2,4,6-tris(1phenyl-1H-tetrazolylsulfanylmethyl)mesitylene (TPTM) has been synthesized through a facile procedure. As expected, it adopts an all-syn cylindrical configuration, thereby delimiting an inner cavity. To explore the solvatomorphism and inclusion behavior of TPTM, a series of organic and inorganic species were employed as guests to afford 17 inclusion compounds (1, 2, 3a-3f, 4a-4i) that can be classified into four distinct forms (forms I-IV), under similar conditions. These compounds were characterized by singlecrystal and powder X-ray diffraction, and ¹H NMR studies. In compound 1 with form I, one foot of a TPTM molecule inserts into the cavity of an opposite TPTM molecule to form a dimeric

"hand-shake" motif with one acetonitrile molecule occupying the void. Compound 2 with form II contains three types of capsule-shaped dimers, each of which holds a CH₂Cl₂ molecule as the guest. In compounds 3a-3f with form III, each pair of TPTM molecules interdigitates to form a capsule-shaped dimeric unit accommodating a guest molecule in the endo-cavity. In compounds 4a-4i with form IV, each TPTM molecule makes contact with three nearby TPTM molecules in a "self-including" manner to generate a graphite-like organic layer, and

Keywords: host-guest systems • inclusion compounds • solvatomorphism • tripodal hosts through further superposition to form open hexagonal channels. From the experimental and theoretical results, the intrinsic properties of guest molecules, such as size, shape, and self-interaction, can be regarded as the main factors leading to these solvatomorphism phenomena and the subtle inclusion behavior of TPTM. Thermogravimetric analyses show that the encapsulated guest molecules in these compounds can be evacuated at relatively high temperatures, and this demonstrates the outstanding inclusion capability of TPTM. In addition, for compound 4a with benzene molecules in the channels, reversible exchange of toluene and separation of xylene isomers on single crystals have been observed.

Introduction

Solid-state inclusion compounds, which essentially involve physical immobilization of guest molecules in host cavities or voids between hosts in crystalline form,^[1] have been of importance in the separation of analogues^[2] and enantio-

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mers,^[3] storage of gases^[4] and toxic substances,^[5] stabilization of reactive compounds,^[6] and control of reaction pathways within a confined space.^[7] In recent decades, the development of this field has inspired modern supramolecular design of more elaborate organic host molecules with various structural motifs, such as tri-*o*-thymotide (TOT),^[8] cyclotriveralene (CTV),^[9] calixarenes,^[10] and a series of tripodal host molecules.^[11–13]

One attractive feature of the tripodal host molecule is that the rigid central platform can provide some degree of preorganization with all three binding feet projected in one direction and afford a thermodynamically favored cavity. On the basis of this model, a variety of organic hosts have been developed by using trialkylbenzene cores as rigid platforms connected with straight pendant groups, either rigid^[12] or flexible.^[13] However, the small spacing between the three feet for each trialkylbenzene core precludes large guests from occupying the cavities and limits their applications as



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molecular hosts. Instead of using straight pendant groups, we envisioned that longer bent ones would expand the distance between the three binding feet and also the volume of the predesigned cavities. Moreover, the newly introduced bent pendant groups could be adjusted to a position perpendicular to the central ring plane by selecting proper linker atoms, and thus lead to a structural transformation of the tripodal host from the traditional conical conformation to a cylindrical one (Scheme 1). This modulation would remarkably strengthen the inclusion capability towards larger guests.



Scheme 1. Steric configuration of the substituents of 1,3,5-trialkylbenzene derivatives with straight and bent pendant groups (gray balls represent the volumes of the preorganized cavities).

The phenomenon of polymorphism is attracting significant attention in the chemical and pharmaceutical industries for various reasons.^[14] In particular, some versatile organic host molecules have a pronounced tendency to undergo cocrystallization with a variety of relatively small solvent guest molecules, which generates different forms of inclusion compounds.^[10a] This solvate diversity of a particular host compound is known as solvatomorphism.^[15] Therefore, it is instructive to understand the relationship between the forms of inclusion compounds and the nature of solvent guest molecules, such as size, shape, and self-interaction, for new insights into the inclusion behavior of organic hosts.

As an extension of our work on tridentate thioether compounds,^[16] we chose to attach 1-phenyl-1*H*-tetrazole-5-thiol pendant groups to a mesitylene core to prepare an expanded tripodal host molecule, namely, 2,4,6-tris(1-phenyl-1*H*-tetrazolylsulfanylmethyl)mesitylene (TPTM).^[17] Due to the hydrophobic nature of the protruding phenyl groups and mesitylene core, some cyclic hydrocarbon molecules are regarded as appropriate guests for packing into the cavities or lattices of this new host molecule. Herein we study the dependence of the solvatomorphism of TPTM on the nature of the guest molecules, and present 17 inclusion compounds (**1**, **2**, **3a–3f**, **4a–4i**) with four distinct forms **I–IV**, along with their thermal behavior. Besides these results, reversible guest exchange and selective separation of xylene isomers on single crystals of **4a** were also studied.



Results and Discussion

Synthesis and configuration of TPTM: Treatment of tris-(bromomethyl)mesitylene with 1-phenyl-1H-tetrazole-5thiol in the presence of base under reflux afforded TPTM in high yield. Crystals of **1–4** suitable for single-crystal X-ray analysis were obtained by crystallization from MeCN (1) or dichloromethane (2-4). As predicted, X-ray structure analysis reveals that the TPTM molecules adopt an all-syn u,u,u configuration in all cases (u = up and d = down; there are only two conformations: $u,u,u \equiv d,d,d$ and $u,u,d \equiv u,d,d$), and the pendant phenyl groups are directed towards the same side. To explain the conformational preference, we calculated the relative energies of different conformers at the PBE/ 6-31G* and B3LYP/6-31G* levels. The results indicate that u,u,d conformation lies about 0.7 kcal mol⁻¹ higher than the most stable u,u,u configuration. Despite this relatively slight energy difference, host-guest interactions and close packing may also account for the stabilization of all-syn conformation, which can be concluded from diverse crystal structures of TPTM molecules.

X-ray crystallography and solvatomorphism: In the presence of different guest molecules, we obtained four diverse crystal forms, denoted forms **I–IV**.

Form I: Recrystallization of TPTM from MeCN affords large amounts of colorless block crystals of TPTM₂·MeCN (1), and single-crystal X-ray analysis reveals that 1 crystallizes in the triclinic space group $P\overline{1}$ (form I). As shown in Figure 1, there are two TPTM molecules and one acetonitrile molecule in the asymmetric unit. One foot of a TPTM molecule inserts into the preorganized cavity of the other and thus forms a dimeric "hand-shake" motif. The distances between the hydrogen atoms on the feet (the "plug") and the centers of the mesitylene rings (the "socket") are 2.81 and 3.06 Å (the closest contacts are ca. 2.99 and 2.83 Å), and clearly indicate CH-- π interactions. These offset dimers are arranged by close stacking in the crystal structure, and the small acetonitrile molecule fills the void among them with an interesting $\pi \cdots \pi$ interaction between the CN group and the tetrazole ring (C---centroid and N---centroid distances are 3.22 and 3.29 Å, respectively).

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Figure 1. View of the homodimeric hand-shake dimer of compound 1. The CH-- π and π -- π interactions are represented as dashed lines.

Form II: Slow evaporation of a solution of TPTM in dichloromethane in air afforded colorless hexagonal crystals of TPTM₂·CH₂Cl₂ (**2**), which crystallizes in the trigonal space group $R\bar{3}$ (form **II**). In the structure of **2**, two TPTM molecules are arranged face-to-face to form a capsuleshaped dimer with an interior cavity holding a CH₂Cl₂ molecule as the guest (Figure 2). The unit cell contains three



Figure 2. View of the three kinds of dimeric units in compound **2**. Only one set of disordered fragments of the encapsulated CH_2Cl_2 molecules is shown as space-filling models for clarity.

types of dimeric units in which all of the TPTM molecules adopt a *gauche* conformation with deviation from the strict cylindrical form by rotation of the pendant groups to various extents to accommodate a CH_2Cl_2 guest molecule. Despite the similar inclusion modes, the three types of dimers lying on different crystallographic positions have diverse thermal stabilities, as supported by thermogravimetric analysis (see below).

Form III: When one equivalent of toluene was added to a solution of TPTM in dichloromethane, block crystals of TPTM₂· C_7H_8 (**3a**) were obtained. Single-crystal X-ray analysis showed two independent molecules of TPTM and two

half-molecules of toluene in the asymmetric unit. Thus, two TPTM molecules and their corresponding symmetry-related molecules in compound **3a** interdigitate to form two similar capsule-shaped dimers containing a toluene in each *endo*-cavity. Despite the similarity of the dimeric units to those in **2**, the pendant phenyl groups of TPTM in **3a** are almost perpendicular to the central core, and the whole molecule adopts a more precisely cylindrical configuration than in **2**. As shown in Figure 3, the toluene molecule is sealed in by the hydrophobic walls and interacts with phenyl groups through perceptible CH····π interactions (2.79 and 2.84 Å).



Figure 3. View of the dimeric units of TPTM with cylindrical configuration in **3a**. The encapsulated toluene molecule is shown as a space-filling model and the two positions of its disordered methyl group each with 50% occupancy are represented.

Form IV: Surprisingly, distinct crystalline phase TPTM·C₆H₆ (4a) in trigonal space group $P\bar{3}c1$ was obtained simply by replacing toluene with benzene. Single-crystal analysis reveals only one-third of a TPTM molecule in the asymmetric unit, and it can be expanded to a whole molecule by a threefold rotation axis. As indicated by Figure 4a and b, TPTM molecules are offset in a face-to-face arrangement, and three phenyl feet from opposite diverse TPTM molecules are inserted in the preorganized cavity of each host molecule, in what can be described as a "self-including" manner. Because of its contact with three nearby TPTM molecules, each TPTM molecule can be regarded as a three-connected topological node, resulting in a graphite-like organic layer with hexagonal grids, and further superposition of these organic layers forms hexagonal channels in the presence of guest benzene molecules (Figure 4c). Crystallographic structure solution revealed that one benzene molecule is located at the center of a channel on a threefold rotoinversion axis, and adopts a horizontal mode. Besides, TG analysis and ¹H NMR spectroscopy determine one more highly disordered benzene molecule (Figures S4 and S5 in the Support-

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Figure 4. a) Axial and b) side view of the offset face-to-face arrangement of TPTM in a "self-including" manner. c) Graphite-like layer with hexagonal grids occupied by benzene molecules (hexagonal rings).

ing Information), probably within the solvent-free area of organic layers.

In an attempt to gain a better understanding of what properties of the guest molecules are responsible for the packing mode of crystals, many other guest molecules were employed to explore the inclusion behavior of TPTM. The crystal forms of inclusion compounds with diverse guest molecules are listed in Table 1, the structures of which were characterized by single-crystal X-ray diffraction (Table 2) or X-ray powder diffraction (XRPD) and ¹H NMR spectroscopy (see the Supporting Information).

As shown in Table 1, crystals 3a-3e with form III were obtained when cyclic hydrocarbons such as toluene (C_7H_8), *p*-xylene (PX), phenylethylene (PE), and cyclohexane (C_6H_{12}), as well as THF, were added as guests. X-ray single crystal diffraction and XRPD analyses determined that they are all comprised of capsular dimeric units with corresponding guests and have similar crystal cell parameters (Figure 5). Interestingly, the inorganic, diatomic iodine molecule (I_2) can also be encapsulated in the cavity of a dimeric unit to afford crimson inclusion compound TPTM₂·I₂ (**3 f**, Table 1. The crystal forms of inclusion compounds **1–4** with diverse guest molecules.





Figure 5. View of the dimeric units of TPTM in a) 3b, b) 3c, c) 3d, and d) 3f. The encapsulated guest molecules are *p*-xylene, phenylethylene, tetrahydrofuran, and iodine, respectively. Only one disordered fragment of the guest molecules is shown as a space-filling model for clarity.

Figure S3 in the Supporting Information); this phenomenon reveals the versatile inclusion capability of TPTM.

In contrast, other small organic analogues of very similar size, such as benzene (C_6H_6), pyridine (py), halobenzenes (C_6H_5X ; X=F, Cl, Br, I), α,α,α -trifluorotoluene (TFT), and ferrocene (Cp_2Fe), induced formation of crystal form IV (Figure 6a). In contrast to the horizontal arrangement of the benzene molecules in **4a**, the halobenzene molecules are all arranged along the threefold axes in an approximately upright fashion in **4c–4h**. These halobenzene molecules all show threefold disorder due to their location on threefold symmetry axes; we chose one position of the guest for the

Table 2.	Crystal	data	and	structure	refinements	for	all	the	comp	lexes
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	1	2		3a		3b		3 c		3 d		3 f		
formula	$C_{68}H_{63}N_{25}S_6$	C335H310N120S	30Cl5	5 C ₇₃ H ₆₈ N ₂₄ S ₆		$C_{74}H_{70}N_{24}S_6$		$C_{74}H_{68}N_{24}S_6$		C70H68N24OS6		$C_{66}H_{60}N_{24}S_6I_2$		
$M_{\rm r}$	1422.79	7333.32	7333.32		1473.87		1487.90		1485.88		1453.84		1635.54	
crystal system	triclinic	trigonal	mal		triclinic		triclinic		triclinic		triclinic		triclinic	
space group	$P\bar{1}$	RĪ		$P\bar{1}$		$P\bar{1}$		$P\bar{1}$		$P\bar{1}$		$P\bar{1}$		
a [Å]	13.815(4)	21.8938(5)	938(5)		13.228(8)		13.0908(13)		13.0761(6)		13.198(5)		137(6)	
b [Å]	15.133(5)	21.8938(5)		13.625(8)		13.5630(13)		13.622	13.6229(6)		13.304(5)		13.3168(6)	
c [Å]	18.047(6)	66.196(3)		22.478(13)		22.536(2)		22.4652(10)		22.199(8)		22.1910(10)		
α [°]	78.186(11)	90		91.279(5)		90.560(2)		90.4990(10)		92.334(6)		92.285(2)		
β [°]	75.196(9)	90		94.493(10)		95.241(2)		95.2880(10)		93.410(3)		93.507(2)		
γ [°]	75.301(9)	120		108.253(9)		108.149(2)		108.7250(10)		108.509(5)		108.6050(10)		
$V[A^3]$	3488.7(19)	27479.4(16)		3831(4)		3783.2(6)	3770.8	(3)	3682	(2)	3686	5.5(3)	
Z	2	3		2		2		2		2		2		
$ ho_{ m calcd} [m Mgm^{-3}]$	1.354	1.329		1.278		1.306		1.309		1.311		1.47	3	
$\mu_{\text{calcd}} [\text{mm}^{-1}]$	0.258	0.318		0.237		0.241		0.242		0.247		1.081		
measured reflns	27121	49066		28628		13509		51 996		28727		50755		
unique reflns	15708	15190		17019		7585		17774		1663	9	17259		
R _{int}	0.0277	0.0345		0.0320		0.0268		0.0592		0.023	0	0.08	95	
GOF	1.085	1.088		1.056		1.069		1.154		1.030	1	0.90	5	
$R_1, wR_2 [I > 2\sigma(I)]$	0.0614, 0.1407	0.1150, 0.334	45 0.070		0.1840	0.0973, 0.3029		0.1129	0.1129, 0.3257		0.0697, 0.1824		0.1099, 0.2998	
R_1 , wR_2 (all data)	0.0933, 0.1617	0.1982, 0.436	6 0.0960, 0		0.2079 0.1306,		0.3834 0.2245, 0		, 0.4036	.4036 0.0992, 0.2133		0.2583, 0.3756		
	4a	4 d	4 e		4 f		4h		4i		4 k		4a''	
formula	$C_{13}H_{12}N_4S$	$C_{39}H_{35}N_{12}S_3Cl$	C39H35	$N_{12}S_3Br$	C39H35	$N_{12}S_3I$	C40H35N	1 ₁₃ S ₃	C76H70N24	S ₆ Fe	C35H32.50N1	${}_{2}S_{3}$	$C_{13}H_{12}N_4S$	
M _r	256.33	803.42	847.88		894.87		793.99		1567.80		717.41		256.33	
crystal system	trigonal	trigonal	trigon	al	trigona	ıl	trigonal		trigonal		trigonal		trigonal	
space group	P3c1	$P\bar{3}c1$	$P\bar{3}c1$		$P\bar{3}c1$	$P\bar{3}c1$		$P\bar{3}c1$		$P\bar{3}c1$			$P\bar{3}c1$	
a [Å]	13.0587(3)	13.0884(2)	13.085	9(2)	13.1135	5(19) 13.1288(6		6) 13.0209(2		2) 13.0958(2)			13.0346(4)	
<i>b</i> [Å]	13.0587(3)	13.0884(2)	13.085	3.0859(2) 13		5(19)	13.1288(6)		13.0209(2)		13.0958(2)		13.0346(4)	
c [Å]	27.2749(10)	27.2076(9)	27.229	7.2294(9) 27		7.249(5) 2		27.313(2)		5)	27.2611(9)		27.2151(16)	
$V[A^3]$	4028.0(2)	4036.40(16)	4038.0	38.09(16) 40		.0(12) 4077.1(4008.86(1		4048.91(10)	4004.4(3)	
Z	12	4	4	4		4		2		4			12	
$ ho_{ m calcd} [m Mgm^{-3}]$	1.268	1.322	1.395	.395 1.4		1.465		1.294		1.299			1.276	
$\mu_{\rm calcd} [{\rm mm}^{-1}]$	0.229	0.295	1.219		0.989		0.229		0.403		0.223		0.230	
measured reflns	23176	52011	24025		51911		23203		32234		19724		21591	
unique reflns	3336	3397	3356		3406		3434		3197		3351		3177	
R _{int}	0.0243	0.0791	0.0310	.0310 0.0		0.0546		0.0283			0.0203		0.0321	
GOF	1.105	1.058	1.041		1.087	1.057		1.075		1.150			1.094	
$R_1, wR_2 [I > 2\sigma(I)]$	0.0628, 0.1812	0.0702, 0.2078	0.0921	, 0.2784	0.1485,	0.4782	0.0530,	0.1530 0.0808, 0.2		.2067 0.0616, 0.18		846	0.0562, 0.1646	
R_1, wR_2 (all data)	0.0754, 0.1963	0.1165, 0.2404	0.1137	0.3041 0.1777,		0.5340 0.0654, 0.1667		0.1667	0.1239, 0.2328		0.0705, 0.1958 0		0.0711, 0.1789	

sake of clarity in Figure 6b. As illustrated in Figure 6b, the adjacent phenyl groups of guests inside the channels interact with each other through offset π - π stacking, whereas their neighboring halogen atoms exhibit some halogen--halogen contacts.^[18] Compared with the conventional isotropic van der Waals radii, which are about 3.52 Å for chlorine, 3.70 Å for bromine, and 3.96 Å for iodine,^[19] these interactions ($d_{\text{Cl}-\text{Cl}}$ =4.09, $d_{\text{Br}-\text{Br}}$ =3.72, and $d_{\text{I}-\text{I}}$ =3.89 Å) appear to be quite weak. Besides these halogen-containing guests, the organometallic compound ferrocene also can be included in the one-dimensional channels as a guest to form crystal **4i** (Figure 6c), which shows a characteristic golden color (Figure S3 in the Supporting Information).

When *m*-xylene (MX), *o*-xylene (OX), or mesitylene was used as guests in dichloromethane, we did not obtain inclusion compounds with TPTM and only obtained crystals of compound 2 containing CH₂Cl₂ molecules.

Discussion of inclusion behavior: In general, the above experimental results have shown that for most guests there is a

delicate balance between the structural alternatives of form **III** with dimeric units and form **IV** with open channels. To aid in understanding the subtle inclusion behavior of TPTM, we calculated the bonding energies of thr corresponding guests and capsule-shaped dimeric unit as described for 3a at the 6-31G(d) level (see Table 3).

Primarily, the size of the guest molecules remarkably affects the packing of TPTM. For example, in **1** the CH₃CN molecule is too small to accommodate in capsule-shaped dimers by effective packing compared with the larger CH₂Cl₂ or cyclic hydrocarbons, and thus only occupies the voids among offset TPTM dimers. Another convincing case is mesitylene, which is larger than other benzene derivatives and cannot be packed into the cavities of dimeric units to cocrystallize with the host molecules. Moreover, the calculated bonding energy of 39.45 kcalmol⁻¹ for mesitylene is much higher than that of toluene (-5.38 kcalmol⁻¹), which also agrees with the considerable destabilization of the former.

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Figure 6. a) View of the hexagonal channels occupied by guest molecules in form **IV**. Schematic representations of arrangement of b) (pseudo)-halogen-substituted aromatics (X = F, Cl, Br, I, and CN) and c) ferrocene in the hexagonal channels of form **IV**. The interactions are represented as dashed lines.

Guest	Structure	Bonding energy [kcalmol ⁻¹]	Charge
benzene		-6.183003495	-0.00249
toluene		-5.38308826	-0.03151
<i>p</i> -xylene	\rightarrow	-1.682965505	-0.00414
<i>m</i> -xylene		2.637200509	-0.01447
o-xylene		3.021773777	-0.01111
mesitylene		39.450753	-0.0159
fluorobenzene	⟨F	-6.831962414	0.00019
chlorobenzene	CI-CI	-5.006966296	-0.00533
bromobenzene	Br-Br	-10.51756333	-0.00544
pyridine	N	-6.541004852	-0.00184
tetrahydrofuran	$\langle \circ \rangle$	-7.268890725	0.00257

The shape of the guest is another crucial factor that can determine the final form of the product. For instance, many cyclic compounds, such as THF, cyclohexane, toluene, and even the larger *p*-xylene, can all be encapsulated by the capsular dimer (form III). However, benzene unexpectedly induced formation of crystal form IV with open channels, although its size falls in the range of the above cyclic molecules. Although there is no perceptible directional interaction in this host-guest system, the hexagonal shape of benzene is most probably responsible for the formation of the hexagonal channels in form IV because of the perfect match of their shapes. This hypothesis can also be supported by formation of the same crystal form when using pyridine, which has the same hexagonal shape. Another example of the influence of guest shape is xylene, for which only the linear *p*-xylene can cocrystallize with TPTM in form III, whereas nonlinear o- and m-xylene molecules cannot be enveloped. This fact can be further interpreted by calculated results that the energy of dimeric unit with *p*-xylene is favorable $(-1.68 \text{ kcal mol}^{-1})$, whereas dimeric units with mxylene and o-xylene are energetically unstable (2.64 and $3.02 \text{ kcal mol}^{-1}$, respectively).

As shown in Table 3, theoretical calculations support the existence of stable dimeric units with the halobenzene molecules (the binding energies of C_6H_5X are -6.83, -5.01, and -10.50 kcal mol⁻¹ for X = F, Cl, and Br, respectively), which have comparable sizes and shapes to toluene and *p*-xylene. Significantly, these halobenzenes co-crystallize with TPTM in form IV and cannot be encapsulated by dimers of form III. Further investigations suggest that these different crystal forms are most likely attributable to the distinct selfinteraction of guest molecules. In contrast to the repelling effect between methyl groups of toluene and p-xylene, the above-mentioned halogen---halogen contacts between halocarbon molecules, such as halobenzenes and α, α, α -trifluorotoluene, can offer an attractive effect to make guests adopt an upright array and connect linearly, which leads to formation of open channels in form IV. To examine this, we used benzonitrile as a pseudohalogen-substituted guest to see which crystal form would be formed. Because the CN group can interact with halogen atoms,^[20] benzonitrile should induce formation of form IV similarly to halobenzenes. On the other hand, the benzonitrile molecule with its eight nonhydrogen atoms and an additional unsaturated bond has an obvious structural similarity in size and shape to phenylethylene, which can be packed into the dimeric unit of form III (3c). The final result of formation of form IV (TPTM·BN, **4h**) undoubtedly indicates that in this situation self-interaction of the guest is the decisive factor for inclusion behavior, rather than the guest structure.

As a general trend, it has been observed that guest molecules containing five to eight light non-hydrogen atoms (C, N, or O) are readily encapsulated in the cavities of the molecular dimer to generate form **III**, which results from a favorable energetic effect between host and guest with appropriate sizes. However, shape and self-interaction of guests may also play a decisive role in controlling the final struc-

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ture, and the distinct form **IV** with open channels is obtained in some situations. Therefore, solvatomorphism of host molecules largely depends on the intrinsic properties of guest molecules, such as size, shape, and self-interaction, and these conclusions give new insight into the inclusion behavior of the tripodal host molecules.

Thermogravimetric analysis (TGA): The thermal stabilities of **1–4** were studied by TGA on crystalline samples under an N₂ atmosphere with a heating rate of 10 °C min⁻¹ between room temperature and 500 °C. All TG plots of these inclusion compounds exhibited an abrupt weight loss from about 200 to 215 °C, that is, the TPTM host is stable up to about 200 °C (see Figure S4 in the Supporting Information).

For compound 1, a gradual weight loss of approximately 5.74% from 50 to 120°C corresponds to the loss of the MeCN molecules (calcd 5.60%), which suggests that the packing is not close and guest molecules tend to escape from the voids of the crystal lattice. The TG analysis of 2 indicated three sequential steps of weight loss before collapse of the host: a gradual weight loss of approximately 2.56% initially occurs from 86 to 170°C, and then weight losses of 1.36 and 2.25% in the ranges of 171-178 and 182-190°C correspond to evacuation of the other two kinds of CH2Cl2 molecules (calcd 2.32, 1.16, 2.32%). These stepwise weight losses of diverse thermal stabilization may correspond to the three categories of crystallographic positions of dimers in 2. For compounds 3 with form III, the weight loss up to about 190°C can be assigned to the release of the corresponding encapsulated guest molecules (calcd for 3a: 6.24%, found: 6.02%; calcd for **3b**: 7.12%, found: 7.07%; calcd for **3d**: 4.95, found: 4.91 %; loss of guest and collapse of the TPTM host overlap for **3e**). For these guest molecules packed in dimeric capsules of 2 and 3, the escape processes all require relatively high temperatures and the obvious evacuation usually occurs after about 150°C. Particularly for 2, the encapsulated CH₂Cl₂ has a low boiling point of 40 °C but exceedingly high escape temperatures of about 170 and 180°C. These results are in good agreement with the structures of compounds 2 and 3 and demonstrate the outstanding inclusion capability of the TPTM host molecule.

For compounds 4 with open channels, all guest molecules are completely removed before collapse of the host (calcd for 4a: 5.07 and 5.07%, found: 5.17 and 5.01%; calcd for 4e: 18.51, found: 19.10%; calcd for 4g: 17.44, found: 18.21%). As shown for **4a** in Figure S4 of the Supporting Information, TGA indicates that there are two separate steps of weight loss before collapse of the host at about 200°C, corresponding to loss of two kinds of benzene molecules at 100-123 and 175-195°C. When as-prepared 4a is treated under vacuum for 24 h, the sample undergoes the first loss of benzene molecules at 90 °C, but retains the original structure and the second type of benzene molecules. In contrast, the structure of 4a obviously changes after only 4 h above 105°C, affording a new unknown phase 4x characterized by XRPD patterns, although the ¹H NMR spectrum revealed that the second type of benzene molecules still remained (Figure S5 in the Supporting Information). Unfortunately, resultant opaque material 4x is devoid of single crystallinity, so the use of single-crystal X-ray diffraction for structural identification is precluded. This solid–solid phase transformation of molecular material is very interesting because it may form an active phase that rapidly adsorbs gases under ambient conditions, especially for a synthetic host with a permanent cavity.^[4a,21] Further investigation into the structure and application in gas adsorption of 4x are underway.

Reversible exchange and separation of guests on single crystals: Compounds **4** have about 24% solvent-accessible volume per unit cell,^[22] which is occupied by diverse guest molecules. Additionally, the networks of compounds **4** are expected to have flexibility to some extent because of the large open channels assembled from purely organic molecules only by interdigitated packing. On the basis of these considerations, we tested whether the guests can be exchanged or selectively adsorbed within the channels in the vapor phase under mild conditions.

When single crystals of **4a** containing benzene molecules were exposed to toluene vapor at 30 °C for about 20 d, they retained single crystallinity, and single-crystal X-ray analysis gave crystal cell parameters similar to those of **4a**. However, the ¹H NMR spectrum indicates that the benzene has been completely replaced by toluene in a molar host/guest ratio of approximately 2:1 to generate TPTM•0.5C₇H₈ (**4j**; Figure S6 of the Supporting Information). It is reasonable that toluene cannot afford a compound with 1:1 host/guest ratio as observed in compounds **3c–3h** (Figure 6b) due to the repelling effect between methyl groups of toluene. Interestingly, the crystal transformation between **4a** and **4j** is reversible. Exposing the same batch of crystals **4j** to benzene vapor for about 20 d led to re-adsorption of benzene to afford **4a'** (Figure S6 of the Supporting Information).

Because the channels in 4 can accommodate substituted benzenes in an upright fashion along the channels, separation of linear and branched hydrocarbons, such as xylene isomers, can be envisioned. To explore the separation of xylene isomers in the vapor phase, crystals 4a were exposed to an equimolar mixed vapor of xylene isomers for 20 d at 40 °C. The ¹H NMR spectrum indicated that only the pxylene is adsorbed into the channels, displacing the benzene to generate TPTM-0.25 PX (4k) with an approximately 4:1 molar ratio of host/guest (Figure S6 of the Supporting Information). Also, the X-ray structural analysis confirms guest exchange in the channels and the single-crystallinity of 4k. The crystal transformation between 4a and 4k is reversible, and compound 4a" re-obtained in benzene vapor was characterized by X-ray structural analysis, which indicated that the guest exchange process could take place in a reversible single-crystal to single-crystal manner. Apparently, this selective adsorption is due to the diameter of the hexagonal channel, which can accommodate linear benzene derivatives and exclude nonlinear ones (Figure 7). This property is reminiscent of the inclusion behavior of urea and thiourea clath-

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Figure 7. Schematic representation of the separation of xylene isomers on single crystals of **4a** with hexagonal channels.

rates with appropriately sized hexagonal channels, and has potential applications in the separation of linear and branched hydrocarbons in the petroleum industry.^[2b]

Conclusion

By using the trialkylbenzene core as a rigid platform, new tripodal host molecule TPTM has been synthesized by a facile procedure. Instead of using straight pendant groups, we have introduced longer bent pendant groups to expand the volume of the predesigned cavity. As expected, this molecule adopts an all-*syn* cylindrical configuration in the solid state, as determined by X-ray crystallographic analyses of 17 inclusion compounds classified into four different forms **I**–**IV**. Herein we have focused on form **II**, comprised of capsule-shaped dimeric units, and form **IV** with open hexagonal channels. From the experimental and theoretical results, the intrinsic properties of these guest molecules, such as size, shape, and self-interaction, can be regarded as the main factors influencing the solvatomorphism and inclusion behavior of TPTM.

The capsule-shaped dimeric unit of form **III** can accommodate a variety of guest molecules from aromatic hydrocarbons to the inorganic iodine molecule, which all have proper structures and no obvious self-interactions. In addition, TGA reveals that the escape of guest molecules enclosed in the dimers of form **III** requires very high temperatures, which demonstrates the outstanding inclusion capability of TPTM. Consequently, the versatile and fine inclusion capabilities make this tripodal form **III** host an attractive candidate as a molecular flask for storing labile molecules or a reactor for single-molecule reactions.

On the other hand, form IV with open channels (for 4a) exhibited interesting properties of reversible exchange of toluene and separation of xylene isomers on single crystals,

and these studies will give new insight into the design and application of molecular materials.

Experimental Section

General: All chemicals were of reagent grade, obtained from commercial sources, and used without further purification. XRPD patterns were collected in sealed glass capillaries by using a Rigaku DMAX 2500 power diffractometer with ultra 18 kW Cu radiation. The thermal behavior was analyzed by TGA by using a NETSCH STA-449C thermoanalyzer. ¹H NMR data were collected by using Bruker AVANCE III 400 and 600 spectrometers. ESI-MS was performed by using a Finigan LCQDECA XP MAX ion trap mass spectrometer.

2,4,6-Tris(1-phenyl-1H-tetrazolsulfanylmethyl)mesitylene (TPTM): TPTM was prepared by a modified literature method.^[23] A solution of 1phenyl-1*H*-tetrazole-5-thiol (2.851 g, 16.00 mmol) and potassium carbonate (2.211 g, 16.00 mmol) in MeCN (40 mL) was stirred for 15 min, and tris(bromomethy1)mesitylene (1.995 g, 5.00 mmol) in dichloromethane (10 mL) was then added slowly. The mixture was stirred vigorously at RT for 24 h and then heated to reflux for 2 h. After evaporation to dryness under vacuum, the solid was added to deionized water (100 mL), and the resultant white precipitate was collected by filtration, washed several times until the pH of the filtrate was 7, dried under vacuum at 90°C, and recrystallized from MeCN to give TPTM (2.473 g, ca. 71.6% yield). ¹H NMR (CDCl₃, 25°C): δ = 7.54–7.59 (m, 15H), 4.77 (s, 6H), 2.52 ppm (s, 9H); ESI-MS: *m/z* (%): 691.6 (10) [*M*+H]⁺, 713.6 (100) [*M*+Na]⁺, 729.3 (35) [*M*+K]⁺ (see the Supporting Information).

TPTM₂·MeCN (1): Slow evaporation of a solution of TPTM (69.1 mg, 0.1 mmol) in MeCN (10 mL) in air afforded a large number of colorless crystals after 48 h (yield: 95%).

TPTM₂-CH₂Cl₂ (2): TPTM (69.1 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (10 mL), and slow evaporation of the solution in the air gave a large amount of colorless hexagonal crystals after 24 h (yield: ca. 99%).

TPTM₂·C₇H₈ (3a): TPTM (69.1 mg, 0.1 mmol) was dissolved in CH_2Cl_2/C_7H_8 (1:1; 10 mL), and colorless block crystals were obtained after slow evaporation of the mixture in air for 24 h (yield: ca. 94%).

TPTM₂·PX (3b): The synthesis was similar to that of **3a**, except that toluene was replaced by *p*-xylene (PX). Colorless block crystals were obtained after slow evaporation for 24 h (yield: ca. 92%).

TPTM₂·PE (3c): The synthesis was similar to that of **3a**, except that toluene was replaced by phenylethylene (PE). Colorless block crystals were obtained after slow evaporation for 24 h (yield: ca. 97%).

TPTM₂·THF (3d): The synthesis was similar to that of 3a, except that toluene was replaced by THF. Colorless block crystals were obtained after slow evaporation for 24 h (yield: ca. 95%).

TPTM₂·C₆H₁₂ (3e): The synthesis was similar to that of **3a**, except that toluene was replaced by cyclohexane (C₆H₁₂). Colorless block crystals were obtained after slow evaporation for 24 h (yield: ca. 95%).

TPTM₂·I₂ (3 f): TPTM (69.1 mg, 0.1 mmol) and I₂ (126.9 mg, 0.5 mmol) were dissolved in CH₂Cl₂ (10 mL). After evaporation to dryness, the resultant solid was washed three times with ethanol to remove residual iodine, affording crimson block crystals (yield: ca. 88%).

TPTM·C₆H₆ (4a): The synthesis was similar to that of **3a**, except that toluene was replaced by benzene (C_6H_6). Colorless hexagonal crystals were obtained after slow evaporation for 24 h (yield: ca. 96%).

TPTM·py (4b): The synthesis was similar to that of **3a**, except that toluene was replaced by pyridine (py). Colorless hexagonal crystals were obtained after slow evaporation for 24 h (yield: ca. 96%).

TPTM-C₆H₆F (4c): The synthesis was similar to that of **3a**, except that toluene was replaced by fluorobenzene (C₆H₆F). Colorless hexagonal crystals were obtained after slow evaporation for 24 h (yield: ca. 93%). **TPTM-C₆H₆Cl (4d)**: The synthesis was similar to that of **3a**, except that toluene was replaced by chlorobenzene (C₆H₆Cl). Colorless hexagonal crystals were obtained after slow evaporation for 24 h (yield: ca. 95%).

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TPTM-C₆H₅Br (4e): The synthesis was similar to that of **3a**, except that toluene was replaced by bromobenzene (C₆H₅Br). Colorless hexagonal crystals were obtained after slow evaporation for 48 h (yield: ca. 96%).

TPTM·C₆H₅I (**4 f**): The synthesis was similar to that of **3a**, except that toluene was replaced by iodobenzene (C_6H_5I). Colorless hexagonal crystals were obtained after slow evaporation for 48 h (yield: ca. 98%).

TPTM-TFT (4g): The synthesis was similar to that of **3a**, except that toluene was replaced by α,α,α -trifluorotoluene (TFT). Colorless hexagonal crystals were obtained after slow evaporation for 48 h (yield: ca. 94%).

TPTM·BN (4h): The synthesis was similar to that of **3a**, except that toluene was replaced by benzonitrile (BN). Colorless hexagonal crystals were obtained after slow evaporation for one week (yield: ca. 95 %).

TPTM-0.5 Cp₂Fe (4i): The synthesis was similar to that of **3 f**, except that I_2 was replaced by ferrocene (Cp₂Fe). Colorless hexagonal crystals were obtained after slow evaporation for 48 h (yield: ca. 86%).

TPTM-0.5 C_7H_8 (4j): Single crystals of 4a were exposed to toluene vapor at 30 °C for about 20 days, and the resultant crystals that retained single crystallinity were collected (yield: 100%).

TPTM-0.25 PX (4k): Single crystals of **4a** were exposed to an equimolar mixed vapor of *p*-xylene, *m*-xylene, and *o*-xylene at 40 °C for about 20 days, and the resultant crystals that retained single-crystallinity were collected (yield: 100%).

X-ray data collection and structure determination: Data for 1, 3a, and 3d were collected by using a Rigaku Mercury CCD-based diffractometer with graphite-monochromated Mo_{Ka} radiation ($\lambda = 0.71073$ Å) by using the ω -scan mode at 293 K. All other data were collected by using a Bruker Smart APEX II CCD-based diffractometer. An absorption correction was applied by using the SADABS program.^[24] The structures were solved by direct methods and refined on F^2 by full-matrix leastsquares techniques by using the SHELXTL-97 program package.^[25] The ordered atoms in each structure were refined with anisotropic displacement parameters, whereas hydrogen atoms were placed in idealized positions and allowed to ride on the relevant carbon atoms. Crystallographic data for 1-4 are summarized in Table 2. CCDC-787266 (1), -787267 (2), -787268 (3a), -787269 (3b), -787270 (3c), -787271 (3d), -787272 (3f), -787273 (4a), -787275 (4d), -787276 (4e), -787277 (4f), -787278 (4h), -787279 (4i), -787280 (4k), and -787274 (4a") contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Because of the very large thermal motion and disorder of the guests in the cavity and lattice of host molecules, the diffuse residual electron density was usually difficult to model accurately and thus a number of restraints were applied to these molecules. Therefore, no attempt was made to locate the hydrogen atoms of guest molecules, and the disordered nonhydrogen atoms were refined isotropically. Also, large differences in the U_{eq} values between neighboring non-hydrogen atoms and some irregular bond lengths could be ascribed to the mobility of the guests. For compound **3c**, some of the non-hydrogen atoms of TPTM were refined isotropically due to the relatively poor quality of the crystal. For compounds **4a**, **4a**", and **4k**, there was significant void space and diffuse residual electron density that could not be accurately assigned in a chemically meaningful way.

Theoretical calculations: We performed a density functional study to investigate the interactions between the TPTM host and the guests. The capsular dimeric unit of two host molecules and one guest molecule were extracted from the crystal structure of **3a** for modeling. The calculation was carried out by using the PBE^[26] density functional at the 6-31G(d) level implemented in Gaussian 03.^[27] The skeleton of the host was fixed to represent the environment of the crystal. All the structural parameters of the guests and the hydrogen atoms in the host were optimized to give the binding energies E_{b} , listed in Table 3. Most of the binding energies are negative, that is, most of the interactions between host and guest are energetically favorable. However, the interactions for *m*-xylene, *o*-xylene, and especially mesitylene are endothermic. There is no noticeable orbital interaction between host and the guest, and the weak charge transfer is

responsible for the weak interaction. The charges on guests are also listed in Table 3.

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