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Distinct Guest-Dependent Changes in Arrangements of a Fluorophore and the Corresponding Emission Modes in a Ternary System: Transcription and Translation of Guest Molecular Information

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In order to prepare novel molecular arrangements of a fluorophore that result in new solid-state fluorescence properties, we fabricated a ternary system consisting of anthracene-2,6-disulfonic acid (ADS), aliphatic primary amines and guest molecules as a fluorophore, arrangement-controlling parts and molecular information sources, respectively. The system consisting of ADS, (*rac*)-*s*-butylamine and 1,4-dioxane yielded a novel zigzag arrangement of anthracene moieties that gave rise to a rare emission mode. Subsequent screening of the amines and guests in the ternary system suggested that a relationship exists among the molecular information source, the zigzag arrangement and the rare emission mode. Namely, molecular information of 1,4-dioxane is transcribed to the zigzag arrangement, and the arrangement is translated into the excimer-like emission. Interestingly, the relationship appears to mimic that found in DNA. In addition, transcription of the molecular information requires the appropriate shape and size of void spaces formed by ADS and (*rac*)-*s*-butylamine. From these observations, the zigzag arrangement and the corresponding rare emission mode is specific for the system of ADS, (*rac*)-*s*-butylamine and 1,4-dioxane.

Design and creation of novel arrangements of a fluorophore in the solid-state should bring about their new solid-state fluorescence properties and subsequently sophisticated materials.[1,2] In addition, novel arrangements should yield not only enhanced fluorescence intensity but also different emission modes in the solid-state, i.e., excimer, monomer, and exciplex.[3,4] For example, Matsumoto and Oshita have reported a rare emission mode for pyrene in the crystalline state, that is, a solid-state monomer emission from discrete pyrene, which is achieved by intercalation of pyrene into layered polymer crystals, although pyrene exhibits excimer-like emission in the crystalline state.[4]

So far, the creation of the arrangements have been mainly achieved by modifying the fluorophores.[5–7] Modifications by organic syntheses is effective; however, it can be time-consuming and expensive due to the following problems. First, it is difficult to predict the arrangements from the components.[8,9] Second, the actual influence of the arrangements on the solid-state fluorescence properties is not well understood. Third, certain modifications may require tedious syntheses. On the other hand, we have reported organic salts of anthracene-2,6-disulfonic acid (ADS) with aliphatic primary amines as a tunable solid-state fluorescence system.[10] This system is a convenient method for tuning the arrangements of anthracene moieties and solid-state fluorescence properties by altering the amines.

Each component in such a binary system contributes to the tuning of the arrangements and the properties; ADS and the amines act as a fluorophore and arrangement-controlling parts, respectively. The system should be appropriate for an investigation of a structure–property relationship because high-throughput screening of the arrangements and properties is possible. However, the arrangements obtained by the binary system are not drastically different from those of anthracene derivatives in the Cambridge Structural Database (CSD) up to now. This is due to the limitations in controlling the arrangement, that is, the deficiency of molecular information sources (e.g., chirality, hydrogen-bonding capacities, steric demands, electrostatic properties, hydrophilic or hydrophobic characters, and metal-ion binding capabilities)[11] in the binary system. Consequently, we considered that novel arrangements might be possible by introducing a heteroatom-containing component as another source of the molecular information to the system. Recently, we have developed a ternary system consisting of ADS, (*rac*)-*s*-butylamine (**1**) and guests as a fluorophore, an arrangement-controlling part and molecular information sources, respectively. As a result, the utilization of 1,4-dioxane as the guest has yielded a novel zigzag arrangement of anthracene moieties and a rare emission mode.[12] In this paper, for elucidation of a relationship between the molecular information and the zigzag arrangement, we prepared two kinds of the systems as shown in Scheme 1. System I was composed of ADS, **1**, and guest molecules, aiming to investigate the effect of the molecular information of the guests on the arrangements of anthracene moieties (Scheme 1a). System II consisted of ADS, aliphatic primary amines, and 1,4-dioxane in order

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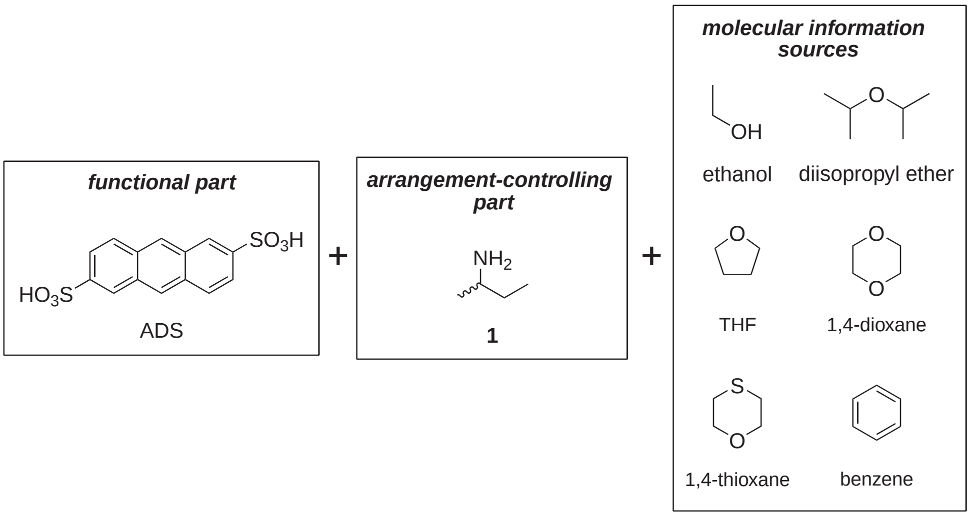
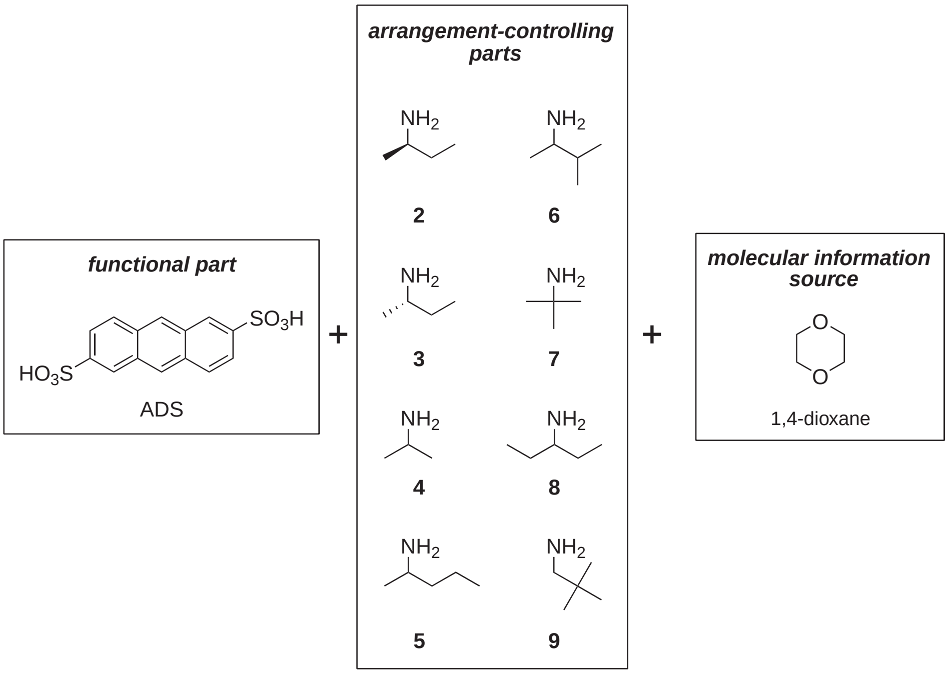
a) **System I**



b) **System II**



Scheme 1. Chemical structures of System I (ADS•**1**•guests) and II (ADS•**amine**•1,4-dioxane).

to investigate suitable systems that effectively utilize the molecular information of 1,4-dioxane (Scheme 1b). These investigations suggest that the zigzag arrangement is achieved by a transcription and a translation of guest molecular information in the crystals.

Results and Discussion

Crystal Structures of System I. In order to investigate the effects of the molecular information of the guests on the arrangements, the following molecules were utilized as the guests: ethanol, diisopropyl ether, tetrahydrofuran (THF), 1,4-dioxane, 1,4-thioxane, and benzene (Scheme 1a). As summarized in Table 1, recrystallization of the salt ADS•**1** from mixtures of methanol and the corresponding guest gave desirable ternary systems ADS•**1**•1,4-dioxane, ADS•**1**•1,4-thioxane, and ADS•**1**•benzene in a molar ratio of 1:2:1. The other candidate molecules were not included into the salt ADS•**1**, and the resulting crystals show a guest-free structure consisting of ADS and **1**. The guest-free structure was constructed of alternating stacks of three segregated layers of ADS, **1**, and hydrogen-bonding network, and involved a two-dimensional herring-bone arrangement as reported in the literature[13] (similar molecular packing diagram is depicted in Fig. 2f). The X-ray crystallographic parameters are summarized in Table 2.

X-ray crystallographic studies showed that a common framework is observed in the ternary systems as shown in

Table 1. Screening of the Guests as Molecular Information Sources in System I

Entry	Arrangement-controlling	Recrystallization solvents	Composition	Arrangement
1	**1**	ethanol	1(ADS)•2(**1**)	herring-bone
2	**1**	methanol/diisopropyl ether	1(ADS)•2(**1**)	herring-bone
3	**1**	methanol/THF	1(ADS)•2(**1**)	herring-bone
4	**1**	methanol/1,4-dioxane	1(ADS)•2(**1**)•1(1,4-dioxane)	zigzag
5	**1**	methanol/1,4-thioxane	1(ADS)•2(**1**)•1(1,4-thioxane)	flipped-parallel
6	**1**	methanol/benzene	1(ADS)•2(**1**)•1(benzene)	flipped-parallel

Table 2. X-ray Crystallographic Parameters

	ADS•**1** •1,4-dioxane	ADS•**1** •1,4-thioxane	ADS•**1** •benzene	ADS•**6** •1,4-dioxane	ADS•**9** •1,4-dioxane	ADS•**2**	ADS•**3**
Formula	$C_{26}H_{40}N_2O_8S_2$	$C_{13}H_{20}NO_{2.50}S_{1.50}$	$C_{14}H_{19}NO_3S$	$C_{14}H_{21}O_4NS$	$C_{28}H_{44}N_2O_8S_2$	$C_{11}H_{16}NO_3S$	$C_{11}H_{16}NO_3S$
Formula weight	572.73	278.40	281.37	299.38	600.78	242.31	242.31
Crystal system	triclinic	triclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	Pn	$P2_1$	$P2_1$
a/Å	10.389(2)	5.6042(9)	5.554(1)	5.6576(1)	5.727(1)	10.615(1)	10.542(2)
b/Å	11.020(2)	10.207(1)	10.241(2)	10.5930(3)	14.907(2)	6.1824(9)	6.189(1)
c/Å	14.128(2)	14.106(2)	13.571(3)	13.7164(3)	17.971(3)	18.789(3)	18.602(4)
α/degree	88.08(1)	74.48(1)	76.31(2)	75.161(2)	90	90	90
β/degree	73.29(1)	78.50(1)	78.81(2)	78.925(2)	96.17(2)	97.60(1)	97.49(2)
γ/degree	69.02(1)	75.38(1)	75.28(2)	73.429(2)	90	90	90
V/Å^3	1442.2(4)	744.7(2)	717.9(3)	755.31(3)	1525.3(5)	1222.3(3)	1203.3(4)
Z	2	2	2	2	2	4	4
D_{calcd}/g cm^{-3}	1.319	1.241	1.301	1.316	1.308	1.317	1.337
No. of unique reflections	4891	2535	2395	2615	2738	2446	2178
No. of observed reflections	15649	8269	6271	6404	15878	10713	10310
$R1/Rw$	0.0870 /0.2231[a]	0.1398 /0.4171[a]	0.1371 /0.3264[a]	0.170 /0.420[a]	0.0807 /0.2000[a]	0.0795 /0.2153[a]	0.109 /0.300[a]
GOF	2.141	1.636	3.259	3.33	1.574	1.624	2.443
2θ max					136.4	136.3	136.4
Reflection/para.	11.37	12.68	10.42	14.45	7.56	8.46	2.12
Temperature/°C	−60	−60	−180	−60	−60	−60	−180

a) $wR_2 = [\Sigma w(F_0^2 - F_C^2)^2/\Sigma_w(F_0^2)^2]^{1/2}$ (for all data).

Fig. 1c. In order to elucidate effects of the guests, we examined the way that the common framework is constructed through non-covalent interactions step by step, as shown in Figs. 1a–1c.[14] The components of the salts form a one-dimensional arrangement via a one-dimensional hydrogen-bonding network (Fig. 1a). In this case, the substituents on the amines were in opposite directions in the network (Fig. 1a). The networks were connected through the anthracene backbones to the organic layer (Fig. 1b). The layers stacked to yield a framework with one-dimensional void spaces, that is, molecular channels (Figs. 1c and 1d). The guests are included into the void spaces, and form their one-dimensional alignments to fit in the spaces. Therefore, it seems that the guests affect the arrangement of anthracene moieties.

Figures 2a–2c show molecular packing diagrams of the crystal structures of system I. Although these systems have a similar one-dimensional arrangement of anthracene moieties, their arrangement was affected by the guests, as shown in Fig. 3. ADS•**1**•1,4-dioxane had a zigzag arrangement (Fig. 3a), while ADS•**1**•1,4-thioxane and ADS•**1**•benzene had flipped-parallel arrangements (Fig. 3b). The structural parameters concerning intermolecular interactions between anthracene moieties are summarized in Table 3. By the basis of the structural parameters, the flipped-parallel arrangements of ADS•**1**•1,4-thioxane and ADS•**1**•benzene are similar, while the flipped-parallel arrangement is constructed by stacking of anthracene moieties in the same orientation, the zigzag one is done by alternately stacking the anthracene moieties in two different orientation. The difference in the arrangements affects a degree of overlap of anthracene moieties (Fig. 3). The overlap areas in flipped-parallel arrangements were clearly smaller than that in zigzag one, meaning that the resulting intermolecular interaction (π/π interaction) between anthracene moieties in the former is larger than that in the latter. From these results, the arrangement manners and the corresponding intermolecular interactions are dependent on the guests. In addition, the zigzag arrangement is drastically different from the arrangements of anthracene derivatives in CSD, while the flipped-parallel arrangements are common.

Solid-State Fluorescence Properties of System I. The

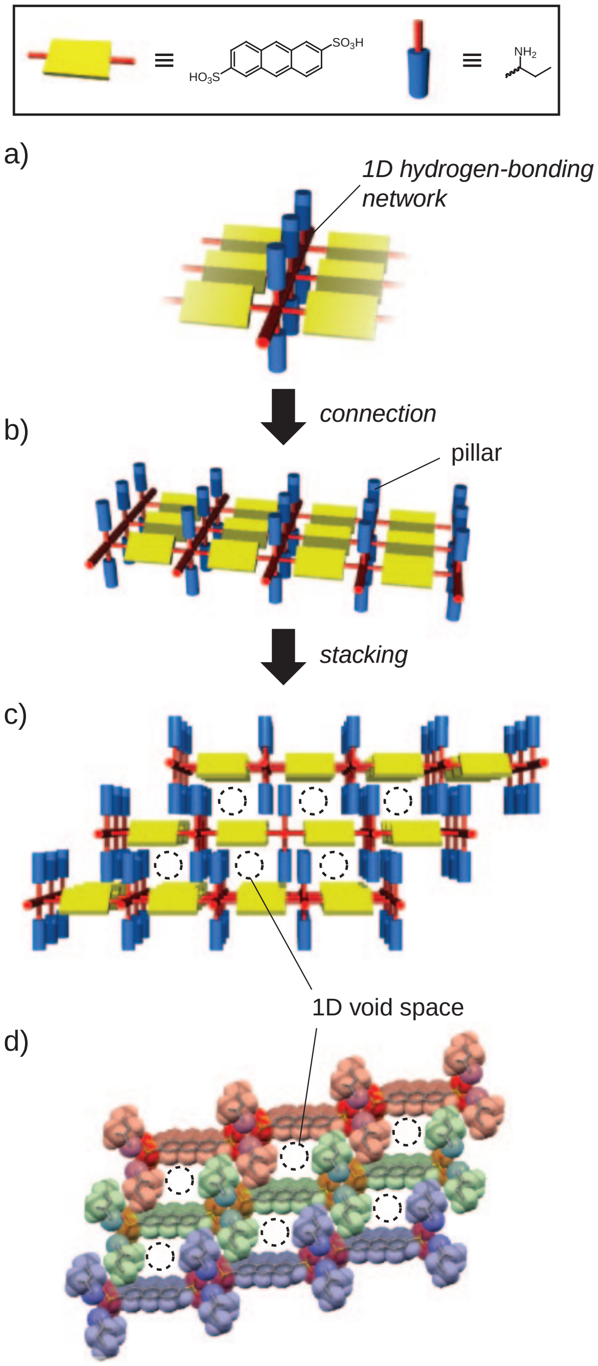


Fig. 1. Schematic representation of construction manners of the common framework through non-covalent interactions step by step. a) The column with one-dimensional hydrogen-bonding network. b) The organic layer formed by connection through the intermediate of anthracene backbone. c) The framework with molecular channels constructed by staking of the layers. b) Molecular packing diagram of the framework consisting of ADS and **1**.

difference in the overlap areas and the intermolecular π/π interactions affects their solid-state emission spectral profiles in the System I, as shown in Fig. 4. The systems ADS·**1**·1,4-thioxane and ADS·**1**·benzene exhibited solid-state emission spectra with vibration structures and an emission maximum at 423 and 427 nm, respectively. Based on published data,[15] these spectra were attributed to emission from the anthracene monomer. On the other hand, ADS·**1**·1,4-dioxane exhibited a structureless spectral profile and an emission maximum at 438 nm. We conclude that the spectrum can be assigned to excimer-like emission due to the structure-less and red-shifted spectrum (Table 4). The emission maximum was observed in a shorter wavelength region than those of the other anthracene excimers,[16] which must be attributed to intermolecular π/π interactions in the zigzag arrangement. The reported arrangements, which exhibit excimer emission, are constructed of a closely parallel stacks of the anthracene moieties.[16] The overlap area in the closely parallel stacks is larger than that in the zigzag arrangement. In addition, another reason for the shorter wavelength must be the molecular structure of ADS. That is to say, the electron-withdrawing groups on ADS must induce the shorter wavelength.

In addition, such an excimer-like emission at room temperature is scarcely found in anthracene derivatives compared to other polycyclic aromatic compounds (pyrene, perylene, and so on).[16,17] In general, excimer emission of the aromatic compound is achieved in a concentrated solution; however, it is difficult to obtain excimer emission from an unmodified anthracene due to very efficient photodimerization to dianthracene in concentrated solutions.[18] Additionally, anthracene displays monomer emission in the crystalline state. Thus, our system is considered to be of interest as a convenient method for modulating the emission modes by choosing the appropriate molecules.

Role of the Guests. 1,4-Dioxane, 1,4-thioxane, and benzene (six-membered cyclic molecules) were included into the framework of ADS·**1** as the guests, while ethanol, diisopropyl ether (chain ones), and THF (five-membered cyclic one) were not. In addition, the included guests appeared to determine the arrangement of anthracene moieties, and the resultant arrangement affected the solid-state emission modes. In System I, 1,4-dioxane is essential for the zigzag arrangement and the corresponding excimer-like emission. As shown in Fig. 5, 1,4-dioxane column was arranged in an alternating face-to-edge alignment, where 1,4-dioxane were perpendicular and parallel to the *ab* plane through intermolecular CH/O interactions between 1,4-dioxane molecules. The anomalous alignment acts as a template for the zigzag arrangement of anthracene moieties. In the zigzag arrangement, the anthracene moieties were arranged through CH/O interactions between hydrogen atoms of anthracene moieties at 9- and 10-positions and oxygen atoms of 1,4-dioxane. In contrast, the columns of 1,4-thioxane and benzene did not have the alternating alignment, but a parallel face-to-face alignment, as shown in Fig. 6, and the alignment acts as a template for the flipped-parallel arrangement. The parallel alignment must be caused by the presence of one or no oxygen atom in these molecules. Due to such a lack of oxygen atoms, there are no CH/O interactions, such as guest-to-guest and guest-to-anthracene moieties, in these molecular packing diagrams. These results suggest that the zigzag arrangement is formed by the following molecular information of 1,4-dioxane: steric demand to be included into the framework of ADS·**1** and capability to form an alternating alignment through the CH/O interactions.

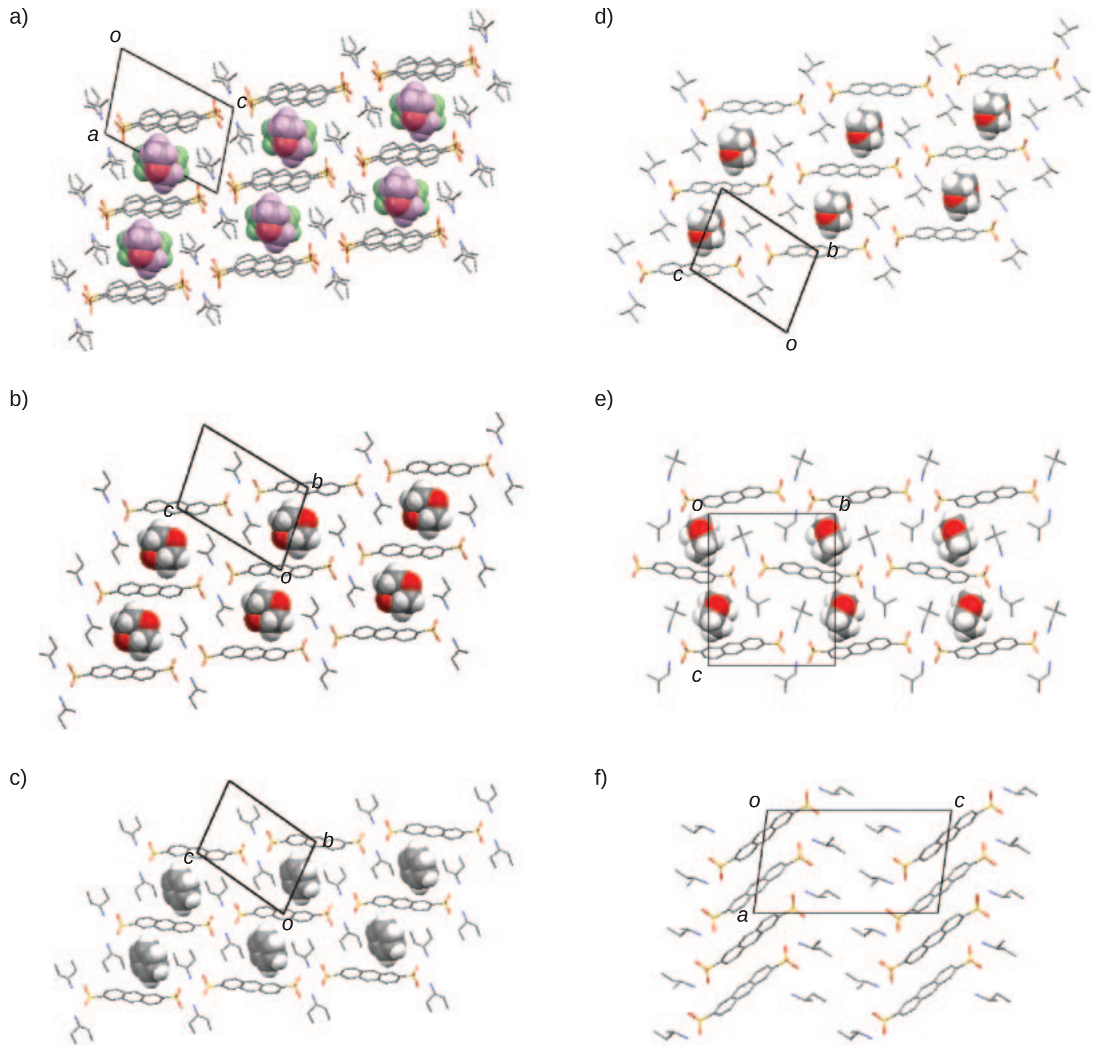


Fig. 2. Molecular packing diagrams of ADS·**1**·1,4-dioxane (a), ADS·**1**·1,4-thioxane (b), ADS·**1**·benzene (c), ADS·**6**·1,4-dioxane (d), ADS·**9**·1,4-dioxane (e), and guest-free crystal of ADS and **2** (f). Purple- and green-colored molecules represent the alternating stacking of two different kinds of the oriented 1,4-dioxane. The guest 1,4-thioxane, the amine **1**, and the guest 1,4-dioxane are disordered in (b), (c), and (d), respectively. Gray, red, blue, and yellow circles and sticks represent carbon, oxygen, nitrogen, and sulfur atoms, respectively.

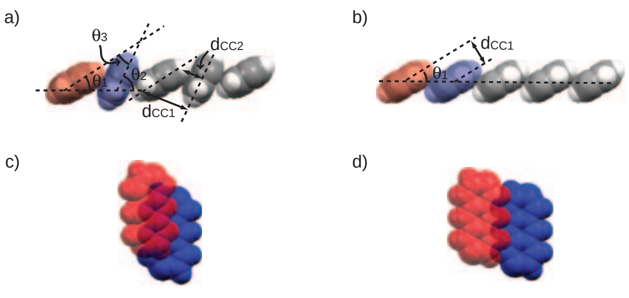


Fig. 3. Molecular arrangement manners of the anthracene moieties in the zigzag (a) and flipped-parallel type (b), and their overlapping motifs (c) and (d), respectively.

Crystal Structures of System II: Role of the Amines as Arrangement-Controlling Parts. The alternating alignment of 1,4-dioxane acts as the template for the formation of the zigzag arrangement, indicating that 1,4-dioxane plays a pivotal role for the formation. Subsequently, we investigated whether the combination of ADS and 1,4-dioxane always yields a zigzag arrangement or not. That is to say, suitable systems for effective utilization of the molecular information of 1,4-dioxane were investigated. As mentioned above, the amines acted as pillars in the framework, meaning that the amines have potential as void space modulators. Thus, we screened the amines similar to **1** as shown in Scheme 1b and Table 5.

When 1,2-dimethylpropylamine (**6**) and neopentylamine (**9**) were utilized, the salt ADS·**6** and ADS·**9** included 1,4-dioxane in a 1:2:1 molar ratio. Figures 2d and 2e depict molecular packing diagrams for ADS·**6**·1,4-dioxane and ADS·**9**·1,4-dioxane, respectively. In these crystals, ADS and the corresponding amines form a similar framework to ADS·**1**. The framework was constructed by stacking of a common layer through the hydrogen-bonding between sulfonate anions and ammonium cations, which generated one-dimensional void spaces to include 1,4-dioxane. In addition, the arrangements of the anthracene moieties is flipped-parallel, which is similar to those of System I (Table 3), and therefore, solid-state fluo-

Table 3. The Structural Parameters Concerning the Arrangement of Anthracene Moieties

System		d_{CC1}/Å	d_{CC2}/Å	θ_1/degree	θ_2/degree	θ_3/degree
I	ADS•**1**•1,4-dioxane	2.840	4.045	28.15	60.86	32.71
	ADS•**1**•1,4-thioxane	2.655	—	29.20	—	—
	ADS•**1**•benzene	2.601	—	28.68	—	—
II	ADS•**6**•1,4-dioxane	2.601	—	28.39	—	—
	ADS•**9**•1,4-dioxane	2.732	—	29.46	—	—

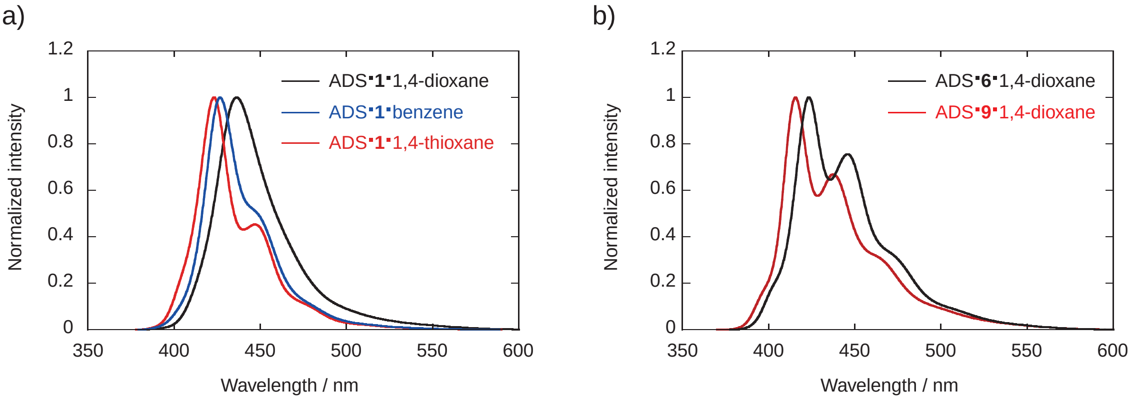


Fig. 4. Solid-state fluorescence emission spectra of System I (a) and II (b). The excitation wavelength was 340 nm in all samples.

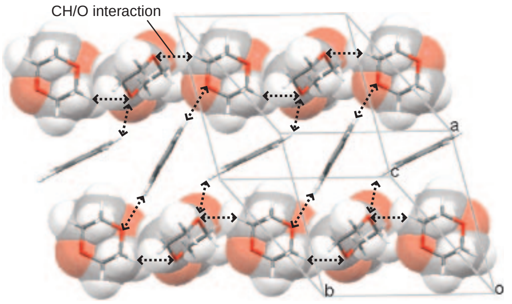


Fig. 5. Structural relationship between the alternating face-to-edge alignment of 1,4-dioxane and zigzag arrangement of anthracene moieties.

Table 4. Solid-State Fluorescence Properties of System I and II

System		λ_{ex}/nm	λ_{em}/nm
I	ADS•**1**•1,4-dioxane	417	438
	ADS•**1**•1,4-thioxane	405	423
	ADS•**1**•benzene	410	427
II	ADS•**6**•1,4-dioxane	403	423
	ADS•**9**•1,4-dioxane	398	416

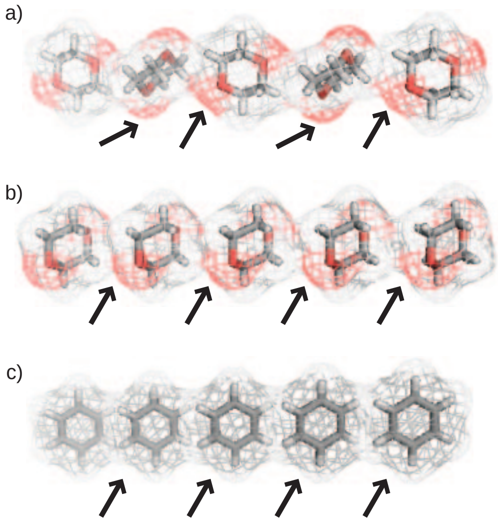


Fig. 6. The alignments of 1,4-dioxane (a), 1,4-thioxane (b), and benzene (c) as the template for the arrangement of anthracene moieties. The black arrows indicate access points of anthracene moieties.

Table 5. Screening of the Amines in System II

Entry	Arrangement-controlling	Recrystallization solvents	Composition	Arrangement
1	**2**	methanol/1,4-dioxane	1(ADS)•2(**2**)	herring-bone
2	**3**	methanol/1,4-dioxane	1(ADS)•2(**3**)	herring-bone
3	**4**	methanol/1,4-dioxane	1(ADS)•2(**4**)	herring-bone
4	**5**	methanol/1,4-dioxane	1(ADS)•2(**5**)	herring-bone
5	**6**	methanol/1,4-dioxane	1(ADS)•2(**6**)•1(1,4-dioxane)	flipped-parallel
6	**7**	methanol/1,4-dioxane	1(ADS)•2(**7**)	herring-bone
7	**8**	methanol/1,4-dioxane	1(ADS)•2(**8**)	flipped-parallel
8	**9**	methanol/1,4-dioxane	1(ADS)•2(**9**)•1(1,4-dioxane)	flipped-parallel

rescence spectra of monomer emission were observed, as shown in Fig. 4b.

In System II, the corresponding amines also act as the pillars of the framework. Therefore, the length and bulkiness of the amines affect the shape and size of the void spaces, which include the guest in the framework. ADS salts with amines **2**–**5** and **7** did not form the framework and void spaces for including 1,4-dioxane. This is because these salts do not provide appropriate void spaces for 1,4-dioxane due to their too small or large spaces. The resulting crystal structures was a stable guest-free structure with a herring-bone arrangement, which is the same as one that was previously reported.[13] Interestingly, even the ADS salts with enantiopure *s*-butylamines, (*R*)- (**2**) and (*S*)- (**3**), did not yield the ternary systems, but the guest-free crystals, as shown in Fig. 2f, meaning that 1,4-dioxane recognizes the racemate of *s*-butylamine. The molecular packing of the salt ADS•**8** was similar to the framework of ADS•**1** (Fig. 1). However, the salt did not possess any void spaces to include 1,4-dioxane as shown in Fig. 7. The absence of void spaces is caused by the substituent on **8**. The long and bifurcated substituent fills the void spaces between the layers consisting of ADS and **8**. ADS•**8** had a one-dimensional structure, due to the formation of common layers and a flipped-parallel arrangement.

The salts ADS•**6** and ADS•**9** formed a framework with void spaces to include 1,4-dioxane, and the shape and size of the void spaces are different from those of ADS•**1**•1,4-dioxane.

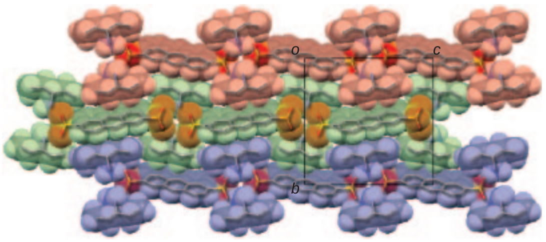


Fig. 7. Molecular packing diagram of the salt ADS•**8**. Red-, green-, and blue-colored molecules represent the respective layers.

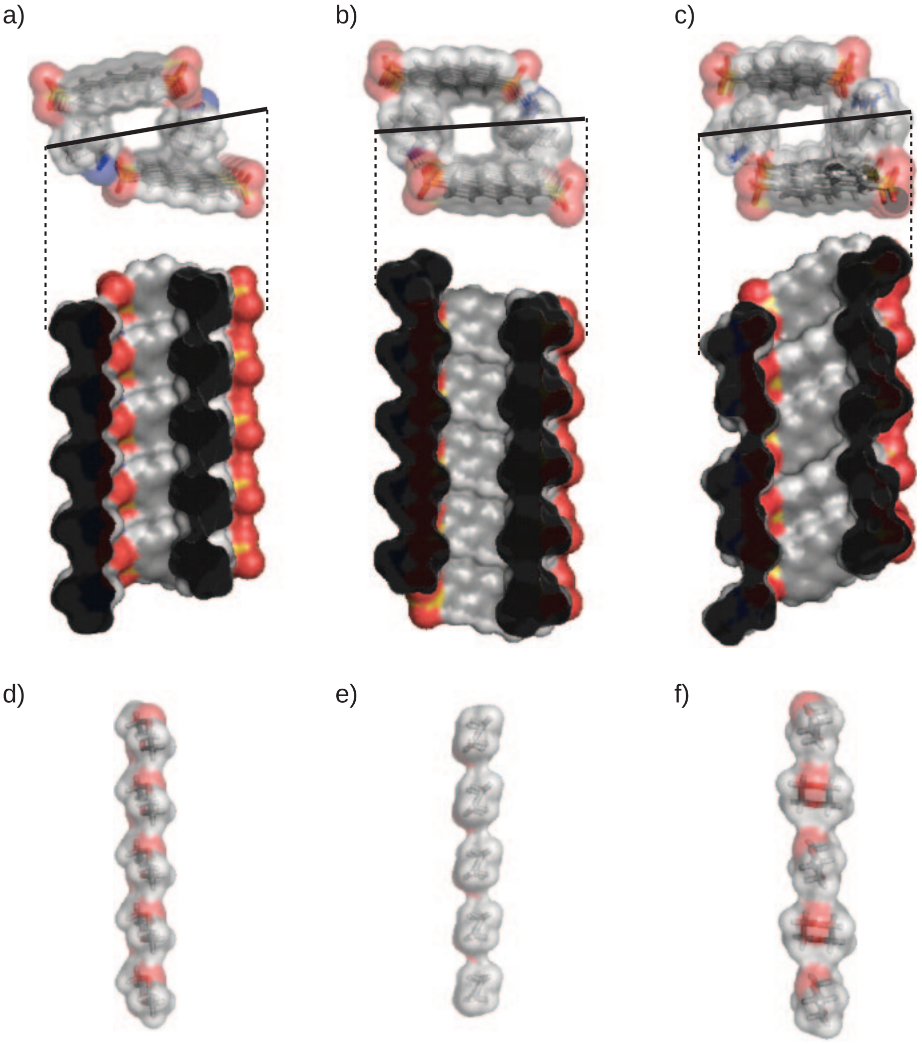


Fig. 8. Solvent accessible surfaces of the void spaces and their tomographies of the frameworks in the crystal structures of ADS•**6**•1,4-dioxane (a), ADS•**9**•1,4-dioxane (b), and ADS•**1**•1,4-dioxane (c), and their alignments of 1,4-dioxane (d–f), respectively.

Table 6. Packing Coefficients of the Selected Systems Including 1,4-Dioxane

System	No. of guest molecules in the unit cell	V_{unit} /Å^{3} a)	V_{cavity} /Å^{3} b)	Proportion of the void space in unit cell/%$^{\text{c)}}$	PC_{cavity} /%$^{\text{d)}}$
ADS•**1**•1,4-dioxane	2	1442.1	259.9	18.0	67.8
ADS•**6**•1,4-dioxane	1	755.3	127.4	16.9	69.2
ADS•**9**•1,4-dioxane	2	1525.3	250.0	16.4	70.5

a) V_{unit} is the total volume of the unit cell from the X-ray crystallographic study. b) V_{cavity} is the volume of void space in the unit cell calculated with a 0.7 Å radius probe. c) Proportion of the void space in unit cell = $V_{\text{cavity}}/V_{\text{unit}} \times 100$. d) PC_{cavity} = (molecular volume of 1,4-dioxane, 88.13 Å^{3}) × (number of guest molecules in unit cell)/$V_{\text{cavity}} \times 100$. The molecular volume of 1,4-dioxane was calculated by using semi-empirical/AM-1.

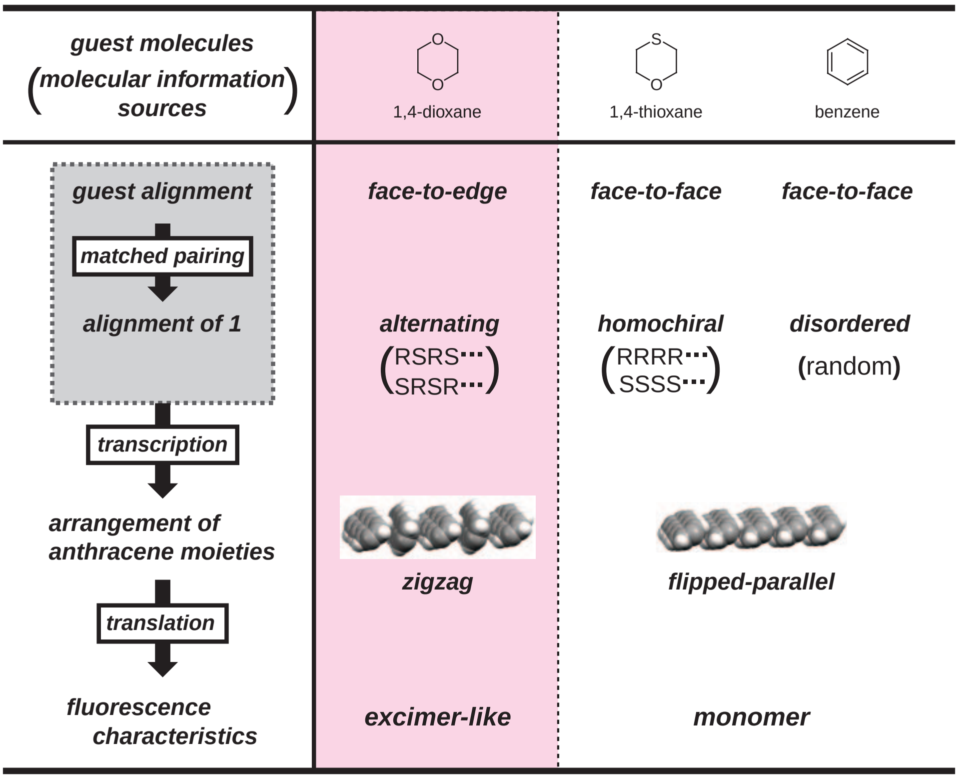
Figures 8a–8c shows the void spaces in the crystal structures of ADS•**1**•1,4-dioxane, ADS•**6**•1,4-dioxane, and ADS•**9**•1,4-dioxane, respectively. As can be seen, ADS•**6**•1,4-dioxane and ADS•**9**•1,4-dioxane formed elongated spaces in comparison to ADS•**1**•1,4-dioxane, which are attributed to the length of their pillars (**6** and **9**). In addition, proportions of the void spaces and packing coefficients of 1,4-dioxane (PC_{cavity}) in these systems suggest that the elongate spaces are tight for 1,4-dioxane compared to the space in ADS•**1**•1,4-dioxane (Table 6). Due to their elongated and tight spaces, 1,4-dioxane formed a one-dimensional parallel edge-to-edge alignment (Figs. 8d and 8e). The parallel edge-to-edge alignment acts as a template for the flipped-parallel arrangement. In contrast, the framework of ADS•**1** allows 1,4-dioxane to be included into larger void space, and therefore, 1,4-dioxane forms an alternating face-to-edge alignment (Fig. 8f), which is a template for the zigzag arrangement as above described. The alternating alignment of 1,4-dioxane is afforded by interdigitation with patterned indented surfaces on columns of **1** as shown in Fig. 8c. The patterned indented surfaces are formed by alternating alignments of the (*R*)- and (*S*)-amines. From these investigations, the formation of the zigzag arrangement requires the appropriate shape and size of the void spaces for the alternating alignment of 1,4-dioxane. Thus, **1** is also essential for the formation of the zigzag arrangement.

Transcription and Translation of Molecular Information of the Guests. From both investigations of System I and II, a combination of ADS, **1**, and 1,4-dioxane is needed for the zigzag arrangement and the corresponding excimer-like emission. The zigzag arrangement is achieved by assembly of two alternating alignments of the amine **1** and 1,4-dioxane. The columns of **1** show the alternating alignment of the (*R*)- and (*S*)-amine (Fig. 8c). The guest 1,4-dioxane also have an alternating face-to-edge alignment through intermolecular CH/O interactions between 1,4-dioxane molecules so that an alignment of 1,4-dioxane is interdigitated with that of **1** (Fig. 8f). The interdigitation of these anomalous alignments results in undulation surfaces toward the arrangement of anthracene moieties (Fig. 5). Along with the undulation surfaces, the anthracene moieties form the zigzag arrangement, which shows the excimer emission.

Moreover, ADS•**1** also forms void spaces that can include the other guests, such as 1,4-thioxane and benzene. Interestingly, the guests determine the alignment manners of **1**, as shown in Scheme 2. ADS•**1**•1,4-thioxane had a homochiral alignment where one column is composed of enantiopure amines, and the resulting (*R*)- and (*S*)-columns were oriented in the crystal evenly. On the other hand, ADS•**1**•benzene had a disordered alignment, in which the columns are composed of (*R*)- and (*S*)-amines in random order. These guest-dependent behaviors of the alignment manners are conducive to the changes in the shape and size of the void spaces. The relationship between the guests and the alignment manners can be regarded as a matched pairing. In addition, the matched pairings determine the arrangement manners of anthracene moieties and concomitant solid-state emission modes (Scheme 2). We think that the processes that relate the guests and emission modes are similar as a transcription and translation of DNA sequences according to the central dogma. In other words, molecular information from the guests is transcribed into the arrangement manners, and the arrangements are translated into the corresponding solid-state emission mode. From these observations, the relationship among the molecular information, the zigzag arrangement and the rare emission mode was elucidated.

Conclusion

Ternary systems consisting of ADS, aliphatic primary amines and guest molecules were designed for the preparation of novel arrangements of anthracene moieties and solid-state fluorescence properties. The system ADS•**1**•1,4-dioxane had a new zigzag arrangement and a rare excimer-like emission. In order to elucidate a relationship between the molecular information and the zigzag arrangement, we prepared two systems: system I (ADS•**1**•guests) and II (ADS•**amines**•1,4-dioxane). These investigations indicated the follows. First, the zigzag arrangement is afforded by the following molecular information of 1,4-dioxane: the steric demand to be included into the framework and the capability to form the alternating alignment through CH/O interaction. Secondly, the zigzag arrangement requires the appropriate shape and size of the void space for the formation of the alternating alignment of 1,4-dioxane. The appropriate void space is achieved only by the combination of ADS and the amine **1**. Therefore, 1,4-dioxane act as a source of molecular information amplified by **1** and transcribed to the arrangement of anthracene moieties. The resulting arrangement is translated to give a rare emission mode. This process explains how arrangement of the components formed and why the fluorophore exhibited new emission abilities in solid-state and the organic solid materials. In addition, this is also a significant result in the area of molecular informatics, since most reports about the transcription of molecular information have involved mainly molecular chirality[19,20] and supramolecular chirality.[21]



Scheme 2. The assembly processes of the alignments of guest, those of **1**, and arrangements of anthracene moieties.

Experimental

General Methods. All chemicals and solvents were commercially available and used without any purification. The potassium salt of anthracene-2,6-disulfonate was prepared according to the published procedure.[22] The salt was converted to the acid form (ADS) by passing an aqueous solution through an ion-exchange column filled with an Amberlite IR 120B NA resin (ORGANO). Organic salts of ADS with aliphatic primary amines were prepared by mixing ADS and the amines in ethanol in a 1:2 molar ratio, and a white precipitation, which was the salt, was obtained as the salt by suction filtration. Crystals were obtained by recrystallization from the solvent as summarized in Tables 1 and 5. Well-refined crystals were used in the investigation of the crystal structures and the photophysical properties.

Crystal Structure Determinations. X-ray diffraction data were collected on a Rigaku R-AXIS RAPID diffractometer with a 2D area detector using graphite-monochromatized Cu Kα radiation ($\lambda = 1.54178$ Å). Lattice parameters were obtained by a least-squares analysis from reflections for three oscillation images. Except for ADS·**1**·1,4-thioxane, direct methods (SIR92)[23] were used for the structure solutions. The structures were refined by a full-matrix least-squares procedure with all the observed reflections based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in idealized positions with isotropic displacement parameters relative to the connected non-hydrogen atoms, and not refined. All calculations were performed with the TEXSAN[24] crystallographic software package. On the other hand, the structure of ADS·**1**·1,4-thioxane was solved by direct methods (SIR2004).[25] The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using the riding model. The structure was refined by a full-matrix least-squares refinement (SHELXL97)[26] with all the observed reflections based on F^2. In the case of ADS·**1**·1,4-thioxane, all calculations were performed with the CrystalStructure[27] crystallographic software package.

1,4-Thioxane and the amine **1** were disordered in the crystal structures of ADS·**1**·1,4-thioxane and ADS·**1**·benzene, respectively. The guest 1,4-thioxane was disordered on an inversion center, and thus, the population of S2, O4, C12, C13, C14, and C15 atoms was divided in half. The terminal methyl group of the amine **1** was disordered, and therefore, the populations of C11 and C12 atoms were divided in half. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-299662, CCDC-299663, CCDC-299661, CCDC-624264, CCDC-624265, CCDC-624266, and CCDC-624267 for compound ADS·**1**·1,4-dioxane, ADS·**1**·1,4-thioxane, ADS·**1**·benzene, ADS·**6**·1,4-dioxane, ADS·**9**·1,4-dioxane, ADS·**2**, and ADS·**3**, respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). The crystallographic parameters are summarized in Table 2.

Solid-State Fluorescence Spectroscopy. Fluorescence spectra measurements were performed by using a FP-6500 spectrofluorometer (JASCO) with an attachment for solid-state fluorescence measurement. The samples for the measurements in the solid-state were encapsulated in a cylindrical cell (JASCO). The excitation wavelength was 340 nm.

Molecular Graphics and Calculations. The solvent accessible surfaces of the columns of guests were rendered from the atomic coodinations of X-ray crystallographic studies by using PyMOL (version 0.99).[28] The volumes of the void spaces to include the guests were calculated from the atomic coordinations by using Free Volume program[29] in Cerius2 (version 4.0) software package.[30] The molecular volume of 1,4-dioxane was calculated by using semi-empirical calculation at the level of AM 1 in SPARTAN '04 (version 1.0.3) software package.[31] The atomic radii were adopted as follows: hydrogen = 1.20 Å, carbon = 1.70 Å, oxygen = 1.60 Å, nitrogen = 1.65 Å, and sulfur = 1.80 Å. The probe radius was fixed at 0.7 Å.

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Supporting Information

Solid-state excitation and emission spectra of the guest-free crystals ADS·**1**, ADS·**2**, and ADS·**3**, solid-state excitation spectra of System I and II, emission spectra of System I in solution, visualization of the void space to include 1,4-dioxane, summary of crystallographic parameters. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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