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Anomalous Anthracene Arrangement and Rare Excimer Emission in the Solid State: Transcription and Translation of Molecular Information

Yuji Mizobe, Mikiji Miyata, Ichiro Hisaki, Yasuchika Hasegawa, and Norimitsu Tohnai*

Department of Material and Life Science, Graduate School of Engineering,
Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

tohnai@mls.eng.osaka-u.ac.jp

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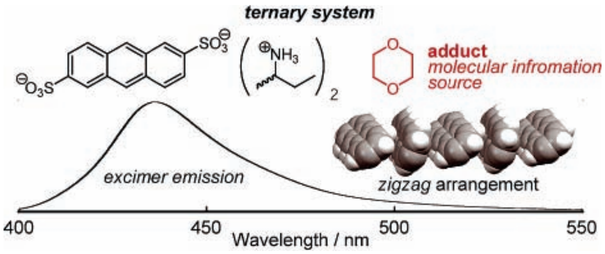
ABSTRACT



A novel molecular arrangement of anthracene moieties and the corresponding rare solid-state excimer emission is obtained by utilization of a ternary system. The system consists of ammonium anthracene disulfonate and adducts, and shows the modulation of the solid-state emission mode depending on the adducts. The adducts act as molecular information sources that are transcribed to the arrangement, and the arrangement is translated into the emission mode. This series of processes might be mimicry of central dogma.

The abilities of organic fluorophores in the solid state have met with increasing interest because of their widespread and direct applications for organic fluorescent materials.[1] In contrast, many organic fluorophores that show fluorescence in solution lose the property in the solid state. As a breakthrough on the problem, tuning of molecular packing and arrangement manners of the fluorophores in the solid state attracts much attention because the arrangements strongly affect the solid-state fluorescence properties.[2,3] In other words, finding a novel arrangement must lead to discovery of a novel ability that is linked to a sophisticated material. On the basis of this strategy, discoveries have so far been afforded by modifications of the fluorophores.[3] However, it is time-consuming and expensive to find new arrangements of the modifications because of the difficulty in predicting the arrangement from the components[4] and the possibility of requiring difficult synthesis.

Recently, we have reported organic salts of anthracene-2,6-disulfonic acid (ADS) with primary amines as a tunable solid-state fluorescence system. The system provides ar-

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rangements of anthracene moieties and concomitant solid-state fluorescence properties depending on the amines. Therefore, the exchanges of the amines must be a more convenient method for the modulation than the modifications of anthracene derivatives, and suitable for the high-throughput screening of the arrangements and properties.[5] From these observations, we can conclude that ADS and the amines act as a functional and arrangement-controlling part, respectively. In fact, the system is composed of two components that play respective roles for the tuning of the arrangement and the properties. The system must be suitable to investigate a structure−property relationship that is a remarkable strategy to design the materials. However, the system has never provided drastic different arrangements in comparison with anthracene derivatives in the Cambridge Structural Database (CSD) until now. Consequently we hypothesize that introduction of another component as a source of molecular information (e.g., steric demand, non-covalent bonding capacity, and electrostatic property)[6] to the system provides new arrangements. Previously, our research group has reported the systematic changes of molecular arrangements and assembly manners by replacement of adducts as the molecular information sources in the steroidal crystals.[7] Thus we designed a ternary system consisting of the salt and adducts as molecular information sources. Indeed, the salt of ADS with racemic *sec*-butylamine ((*rac*)-*s*-BuA) includes adducts (dioxane, thioxane, and benzene) while the salts with enantiopure *s*-BuA ((*R*)- or (*S*)-) do not.

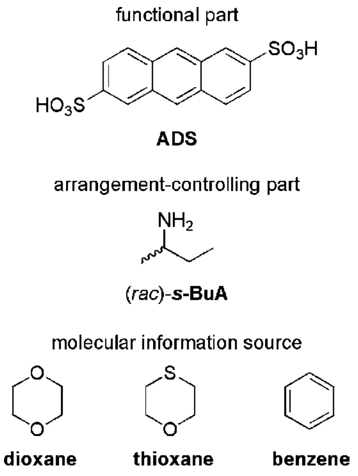

Figure 1. Chemical structures of the functional, arrangement-controlling part and molecular information sources.

Fabrication methods of the system are quite convenient and easy. The potassium salt of anthracene-2,6-disulfonate was prepared according to the published procedure.[8] The salt was converted to the acid form, ADS, by passing it through an ion-exchange column. The organic salt with (*rac*)-*s*-BuA was prepared by mixing ADS and (*rac*)-*s*-BuA in ethanol with a 1:2 molar ratio, and the resulting white precipitation was obtained as the salt by suction filtration. The resulting salt was recrystallized from mixtures of methanol and the corresponding solvents of adducts for preparation of the ternary systems; ADS·(*rac*)-*s*-BuA·dioxane (**S1**), ADS·(*rac*)-*s*-BuA·thioxane (**S2**), and ADS·(*rac*)-*s*-BuA·benzene (**S3**) are shown in Figure 1. The well-refined crystals were used in the investigation of the crystal structures and the photophysical properties.

X-ray crystallographic studies reveal that molecular packing manners of **S1**−**3** are isostructural with each other: the adducts are enclosed in channel-like cavities constructed by ADS columns and (*rac*)-*s*-BuA columns as shown in Figure 2a−c. The corresponding molecular arrangement of

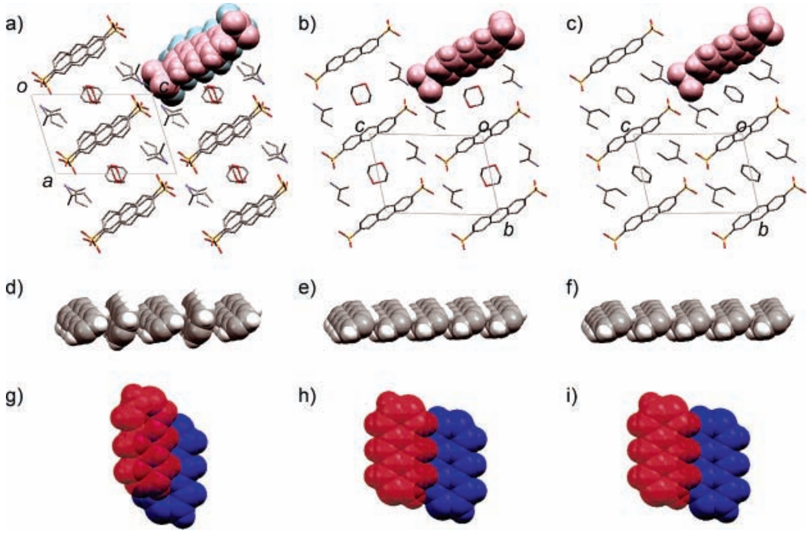

Figure 2. Molecular packing diagram of **S1** (a), **S2** (b), and **S3** (c) from X-ray crystallographic studies. Their arrangements of anthracene moieties (d−f) and stacking motifs of anthracene moieties (g−i), respectively. The guest molecule thioxane and (*rac*)-*s*-BuA are disordered in the crystal structure of **S2** and **S3**, respectively.

anthracene moieties in **S1** is a one-dimensional *zigzag* arrangement (Figure 2d), while those in **S2** and **S3** are a one-dimensional *flipped-parallel* arrangement (Figure 2e−f). The *zigzag* arrangement is a novel one as far as we searched the CSD. On the other hand, the *flipped-parallel* arrangements are commonly observed in the crystal structures of anthracene derivatives. These differences in the arrangements affect a degree of π-overlap of anthracene moieties as shown in Figure 2g−i. The overlap areas in **S2** and **S3** are clearly smaller than that in **S1**, meaning that the resulting intermolecular interaction (π/π interaction) in **S1** must be larger. From these results, the arrangement manner and the corresponding intermolecular interaction between anthracene moieties in **S1** are clearly different from those in **S2** and **S3**.

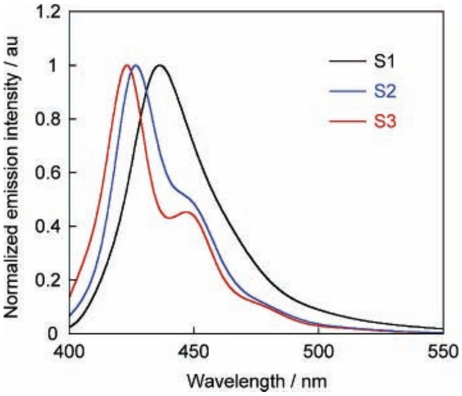

Figure 3. Emission spectra of **S1**, **S2**, and **S3** in the solid state. The excitation wavelength is 340 nm in all samples.

Depending on the difference in the overlap area, their solid-state emission spectral profiles were also distinct as shown in Figure 3. The system **S2** and **S3** displays an emission maximum at 423 and 427 nm with a vibrational band at 448 and 451 nm, respectively. As can be seen by a comparison of these spectra with published data,[9] both spectra can be assigned to emission from the anthracene monomer. On the other hand, **S1** exhibited a structureless spectral profile and an emission maximum at 438 nm. We conclude that the spectrum can be assigned to emission from anthracene excimer because **S1** shows a larger Stoke shift that suggests stronger electronic communication in the excited state (see the Supporting Information). The emission maximum is a shorter wavelength compared to those of common anthracene excimers.[10] The difference may depend on the molecular structure and intermolecular distance as with the published papers.[10,11] In the case of **S1**, the shorter maximum may be caused by the following reasons: electron-withdrawing character of anthracene substituent, i.e., sulfonate group and smaller overlap area of anthracene moieties compared to published data.[10]

From these spectral results, the *flipped-parallel* arrangement shows monomer emission while the *zigzag* arrangement displays excimer emission. As a similar event, rare solid-state monomer emission from anomalous discrete pyrene is achieved by intercalation of pyrene into layered polymer crystal.[12] This example also suggests that the emission mode is modulated by the anomalous arrangement of fluorophores. From another viewpoint, the emission from anthracene excimer at room temperature is quite rare relative to that of other polycyclic aromatic compounds (pyrene, perylene, and so on) due to very efficient photodimerization to dianthracene[13] and unmodified anthracene shows the monomer emission in the solid state. In this connection, there are only a few anthracene derivatives that show the excimer emission.[10] Therefore, our system may be of interest as a convenient method for the modulation of the emission mode upon the choice of adducts.

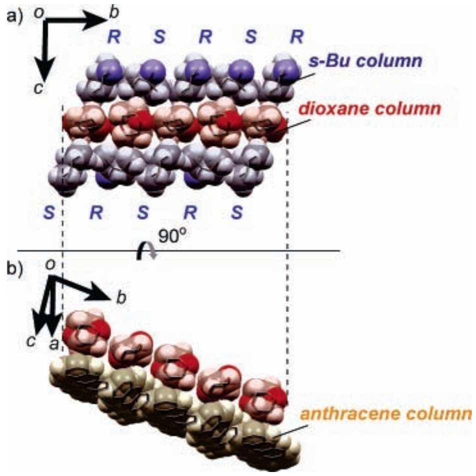

Figure 4. Detail profile of assembly processes of dioxane, (*rac*)-*s*-BuA, and anthracene moieties in the crystal structure of **S1**. (a) The complementary pairing between dioxane and (*rac*)-*s*-BuA; (b) transcription from the complementary pair to arrangement of anthracene moieties.

From detailed investigations of their crystal structures, the adducts determine the arrangements of the anthracene moieties and the corresponding emission mode via assembly processes of the components as described below. Figure 4 shows a detail profile of the processes in the crystal structure of **S1**. The dioxane columns show alternating alignments where dioxane acts parallel and perpendicular to *bc* plane. Along with the alignments, *s*-BuA columns also show alternating ones of the (*R*)- and (*S*)-amine. The intermediation of these anomalous columns results in undulation surfaces

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toward the arrangement of anthracene moieties. Along with the undulation surfaces, the anthracene moieties form the *zigzag* arrangement, which shows the excimer emission. On the other hand, the processes in the crystal structures of **S2** and **S3** are clearly different, and therefore the arrangements and concomitant emission mode are also different. Figure 5 summarizes the comparison of the processes (the alignment of the amines and the arrangement of anthracene moieties) and concomitant emission mode. Interestingly, the adducts determine the alignment of the amines (i.e., alternating, homochiral, and disordered alignment), meaning that the intermediation is regarded as a complementary pairing. We consider that the processes from the adduct to emission mode may be interpreted as a transcription and translation of DNA sequences in central dogma. In other words, molecular information of the adducts is transcribed and translated into the corresponding arrangement and emission mode, respectively. From these observations, the arrangement and concomitant emission mode are modulated by choice of the molecular information of the adduct.

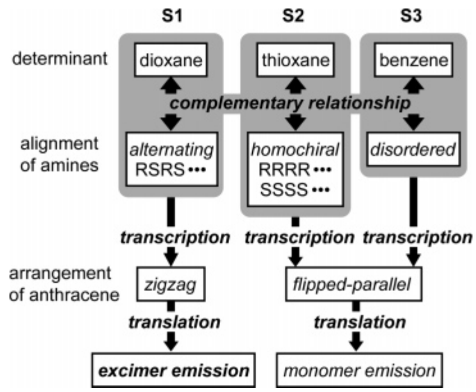

Figure 5. The assembly processes of the components in **S1−3**.

In conclusion, we designed a ternary system consisting of ADS, (*rac*)-*s*-BuA, and adducts that shows the arrangements and concomitant emission mode depending on the adducts. When we used dioxane as the adducts, the new *zigzag* arrangement and the corresponding rare emission from anthracene excimer was obtained. In this system, the adducts act as the sources of molecular information amplified by (*rac*)-*s*-BuA and transcribed to the arrangement of anthracene moieties. The resulting arrangement is translated to emission modes. This is a significant result in perspectives of molecular informatics because most reports about the transcription of molecular information were mainly related to molecular chirality[14] and supramolecular chirality.[15] On the other hand, the systems **S1−3** are shown to be isostructural with each other, and the low-boiling adducts are a determinant of the emission mode. Therefore adsorption and desorption of the adducts might enable us to provide dynamic switching from excimer to monomer emission in the solid state.

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Supporting Information Available: Summary table of crystal structural and solid-state spectral data and crystallographic reports (CIF) of **S1−3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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