Modulation of Solid-state Luminescence Quantum Efficiency Based on CH–O Intermolecular Interaction

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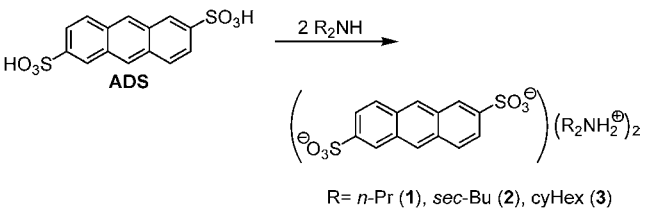
Solid-state luminescence quantum efficiency is modulated drastically by CH–O interaction and packing rigidity of secondary ammonium anthracene-2,6-disulfonate. Appropriate alkyl chains of amines gave small free space and long CH–O distance, resulting in strong luminescence due to suppression of nonradiative decay. This is the first demonstration that CH–O intermolecular interaction has great influence on solid-state luminescence quantum efficiency.

Organic luminescent materials have attracted much attention owing to their potential application in organic devices such as organic light-emitting diodes and solid-state dye lasers.[1,2] Solid-state properties of the materials depend on molecular arrangements as well as molecular structures.[3] In this context, it is known that intermolecular interactions such as π–π interactions and hydrogen bonds, and loose packing derived from molecular arrangements causes luminescence quenching.[4,5a] However, there are few reports that discuss the influence of weak intermolecular interactions (e.g., CH–O or CH–S interactions) on solid-state luminescence efficiency.[6]

Here, we report drastic modulation of the solid-state luminescence quantum efficiency of the same fluorophore, triggered by elaborate regulation of both the packing and the CH–O intermolecular interactions. In our system, alkyl substituents regulated CH–O interaction as well as the packing. This is the first demonstration that slight extension of CH–O distances caused drastic enhancement of solid-state luminescence efficiency in spite of the loose packing.

Organic salts of anthracene-2,6-disulfonic acid (ADS) with secondary aliphatic amines (**1**, di-*n*-propylamine; **2**, di-*sec*-butylamine; **3**, dicyclohexylamine) were employed as a solid-state luminescent material (Scheme 1). ADS was prepared according to the published procedure.[7] Organic salts were prepared by mixing ADS and the amines in ethanol with a 1:2 molar ratio, and the resulting precipitates were obtained as the salts by suction filtration. The salts were recrystallized from methanol or methanol/acetonitrile. The well-refined crystals were used for the investigation of their crystal structures and photophysical properties.

Although all of these crystals showed blue luminescence, their intensities were quite different. Photoluminescence measurements showed that these spectral shapes and emission maximum wavelengths are similar to each other (Figure 1a). However, these solid-state luminescence quantum efficiencies changed drastically: **2** exhibited at least 23-fold increase in quantum efficiency from **3**. **3** hardly luminesces in spite of the same fluorophore. On the other hand, these salts showed almost the same luminescence spectra in methanol solution (Figure 1b). This suggests that the amines do not directly affect the photophysical properties but regulate the packing of the fluorophores, which have profound effect on their photophysical properties.[5,8]



Scheme 1.

X-ray crystallographic studies revealed that their crystal structures are quite similar in arrangements of anthracene moieties[9] (Figures 2a and 2b). These crystals are constructed by alternate stacking of two segregated layers: an ADS layer and an amine layer. Since ADS molecules are completely segregated from each other by the amines, there are no π–π or CH–π interactions between anthracene moieties. Two oxygen atoms of the sulfonate form hydrogen bonds with the amines. These hydrogen bonds are negligible for quenching, because they do not form directly with fluorophores (Figure 2c). Although oxygen atoms of sulfonate in **2** are disordered, this disorder is confirmed to be static disorder according to thermal ellipsoid (see Supporting Information). Therefore, this disorder must have no effect on quantum efficiency. The small difference in their emission maximum wavelength and spectral shape must be attributed to the similar arrangements of the fluorophores.

Free spaces of the crystal, which are responsible for the packing, were regulated by the amines. Calculation by cerius2 showed that more bulky alkyl groups afforded larger spaces (Table 1). Moreover, visualization of the free spaces revealed the movability of the fluorophores in the crystals (Figure 3). Large free space exists around the anthracene ring in **3**, whereas the space disperses in the unit cell of **1**. Therefore, **3** is more likely to undergo vibrational deactivation due to the large free space around the fluorophores.

These results indicate that there is another factor for the

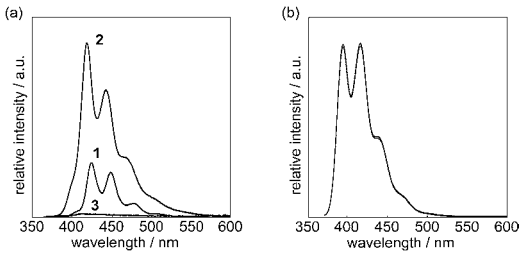


Figure 1. Emission spectra of the salts **1**–**3** in the solid state excited at 350 nm (a) and in methanol solution (10^{-5} M) excited at 340 nm (b). All spectra overlapped in (b).

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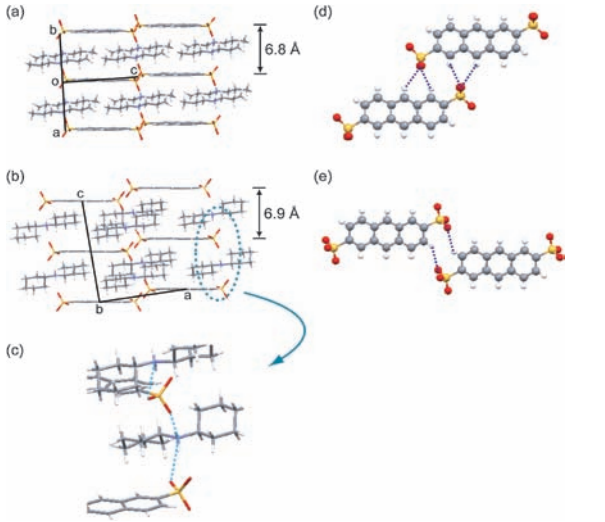

Figure 2. Packing diagram of crystal structure of **1** (a) and **3** (b). Hydrogen-bonding network within dotted circle in (b) is represented by dashed line (c). Schematic pattern of CH–O interactions within ADS layer of **1** and **2** (d), and **3** (e). Short contacts between aromatic hydrogen atoms of ADS and oxygen atoms of sulfonate are represented by dashed lines. Bulky cyclohexyl groups segregated the anthracene moieties within the layer, resulting in subtle change in the manner of CH–O interactions in **3**.

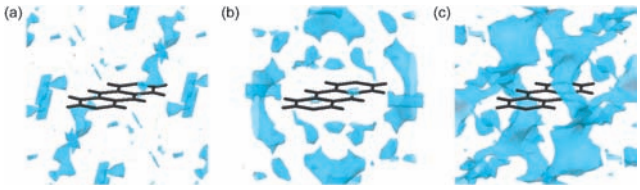

Figure 3. Calculated free spaces around ADS in the crystal structures of **1** (a), **2** (b), and **3** (c). ADS is represented by black stick, and free space calculated with a 0.5 Å probe is done by blue part. For clarity, sulfonic acid groups and amines are omitted.

Table 1. Emission spectral data, calculated free volume, and CH–O intermolecular distances of the organic salts **1–3**

Salt	λ_{em}[a]/nm	Φ_F[b]	V_{free}[c]/V_{unit}[d]/%	CH/O distance/Å
1	425	0.06	7.40	2.40, 2.70
2	419	0.23	9.68	2.66, 2.67
3	414	<0.01	11.69	2.55

[a]Maximum emission wavelength excited at 350 nm. [b]Measurements were performed under deoxygenated conditions. [c]V_{free} is the free volume in a unit cell calculated with a 0.5 Å probe. [d]V_{unit} is the total volume of a unit cell from X-ray crystallographic study.

solid-state luminescence quantum efficiency. Compared with **3**, **1** has more rigid packing, and hence, relatively larger quantum efficiency.[5a] However, surprisingly, **1** showed smaller quantum efficiency than **2** in spite of rigid packing.

In order to resolve this contradiction, we focused on CH–O intermolecular interactions. Even though these salts showed quite similar packing manners, they have a slight but significant difference in CH–O interactions between anthracene moieties and sulfonates (Figures 2d and 2e, and Table 1). The CH–O interactions in **3** should be weakest among these salts owing to fewer CH–O interactions (Figures 2d and 2e). According to the CH···O distances, CH–O interaction in **1** is stronger than that in **2**[6] (the shortest distances is 2.40 Å in **1** and 2.66 Å in **2**, and the average distance is 2.55 Å in **1** and 2.67 Å in **2**). Larger red shifts in emission spectra confirm stronger CH–O interactions.[4a] The CH–O distances and the red shift suggest that the CH–O interaction becomes stronger in the following order: **3** < **2** < **1**. Strong CH–O interactions in **1** should lead to large nonradiative decay. In **2**, steric hindrance of extra methyl groups may interfere with the access of ADS to each other and causes an increase in CH···O distances. Consequently, the CH–O interactions in **2** are weakened and the quantum efficiency is significantly increased. In other words, the smallest propyl groups in **1** afforded the strongest CH–O interactions and, therefore, **1** showed smaller quantum efficiency than **2** despite rigid packing.

In conclusion, this is the first demonstration that CH–O intermolecular interaction has a large influence on solid-state luminescence quantum efficiency. Secondary amines of ammonium anthracene-2,6-disulfonate allowed the regulation of CH–O interactions in addition to packing rigidity, resulting in the drastic modulation of luminescence quantum efficiency from less than 1% to 23%. Such significant difference in the CH–O interaction have not been found in primary ammonium anthracene-2,6-disulfonates. The alkyl chains of moderate size and shape afforded weak CH–O interaction and small free space, resulting in strong luminescence due to the suppression of nonradiative decay. Such tunable systems based on subtle but significant difference in weak intermolecular interaction may have potential application in chemical sensing devices.

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9 These crystallographic data have been deposited with CCDC as nos. CCDC 677878–677880. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.
10 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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