A novel strategy for fluorescence enhancement in the solid-state: affording rigidity to fluorophores packing

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Solid-state fluorescence enhancement was achieved by preparation of rigid packing that was afforded by disposition of benzylamine into tubulate spaces, serving as a powerful and useful strategy for the enhancement.

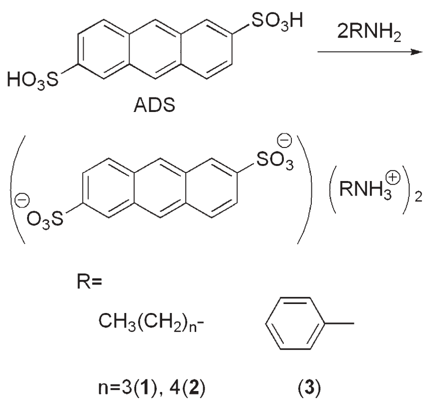
Solid-state fluorescence properties and functions have been attracting interest,[1,2] because solid materials should be particularly useful in applications such as electronic and photonic devices.[2] In addition, a strategy for the enhancement of the solid-state fluorescence plays a pivotal role in the development of a material with sophisticated functions. However, only a few strategies for such enhancement have been reported.[3–5] For example, D. Stalke *et al.* prepared an exciplex composed of an anthracene derivative and toluene which exhibited strong fluorescence.[3] Moreover, the effects of intermolecular interaction in the solid-state on the fluorescence properties were discussed by J. Scott *et al.*[4] and K. Yoshida *et al.*[5] They demonstrated that the fluorescence intensity increased with a decrease in intermolecular interactions (*e.g.* π/π and CH/π interaction). On the other hand, our results were in conflict with these findings[4,5] superficially; one-dimensional arrangements of anthracene moieties showed weaker fluorescence than two-dimensional arrangements, although intermolecular interactions in one-dimensional arrangements were also weaker.[6] In order to resolve this conflict, we focused on the suppression of the distortion of the anthracene ring as a factor for the enhancement. That is to say, the suppression was expected to enhance the solid-state fluorescence of two-dimensional arrangements due to an inhibition of the nonradiative decay process.[7] Indeed, FT-IR spectra suggested that the distortion in two-dimensional arrangements decreased more than that in one-dimensional arrangements.[6] Consequently, we assumed that an increase in rigidity might cause the suppression of the distortion and the concomitant enhancement. In other words, we hypothesized that an increase in the rigidity of packing might be a novel strategy for the enhancement. If the hypothesis is correct, the one-dimensional arrangement surrounded tightly by nonluminous molecules should also exhibit strong fluorescence. In this work, we design a rigid one-dimensional arrangement as proof of the hypothesis and thereby we demonstrate that preparation of rigid packing is also a useful and powerful strategy for the fluorescence enhancement.

The rigid one-dimensional arrangement surrounded by non-luminous molecules was prepared by a disposition of the molecules between one-dimensional arrangements. As the method of the disposition, inclusion phenomena have been well-studied.[8,9] Here we focus on a host framework consisting of anthracene-2,6-disulfonic acid (ADS) and an amino group in the *n*-butylammonium salt (**1**) and the *n*-amylammonium salt (**2**). The framework affords tubulate spaces. Therefore insertion of a rigid component as a substituent of amines into the tubulate space must provide the rigid one-dimensional arrangement. In order to select the fitting amine, we estimated the size of the tubulate space per one amine. According to coordinate data of the crystal structure of **2**, the space was defined as 5.9 Å; 3.9 Å; 9.0 Å (*a*-axis; *b*-axis; *c*-axis). From this size and molecular rigidity requirement, we adopted benzylamine which is defined as 6.5 Å; 3.4 Å; 8.6 Å in order of corresponding length. The *a*-axis of benzylamine is longer than that of the space. It is thought that this problem is resolved by leaning of the benzene ring.

The salts **1**, **2** and benzylammonium salt (**3**) (Scheme 1) were prepared according to a published procedure.[6] The resulting salts were recrystallised from organic solvents (see Table 1) for the purification and yielded the corresponding crystals. The well-refined crystals were used for the investigation of the crystal structures and the photophysical properties.

X-ray crystallographic studies†‡ revealed that their crystal structures were quite similar in the arrangement of anthracene moieties and the position of amines (Fig. 1). As designed, benzylamine was disposed in the tubulate space. In view of the arrangement, it is expected that their fluorescence properties are similar in performance.

However, a dramatic difference in their emission quantum efficiencies was obtained as summarized in Table 1, while their emission wavelengths were little different as shown in Fig. 2. The efficiency increased in the following order: **1** < **2** < **3**. The



Scheme 1

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Table 1 The experimental data and the emission spectral data of the organic salts

	Experimental data		Emission spectral data	
Salt	Recrystallisation solvent	Crystal colour	$\lambda_{em}{}^{a}$/nm	$\Phi_F{}^{b}$
1	methanol–THF	yellow	420	0.01
2	methanol	yellow	419	0.02
3	methanol–water	colourless	424	0.24

[a] The wavelength (nm) of the band assigned to S_0–S_1 emission. [b] The quantum efficiency determined by using anthracene crystal (Φ_F = 0.50) in the solid-state[13] as the standard.

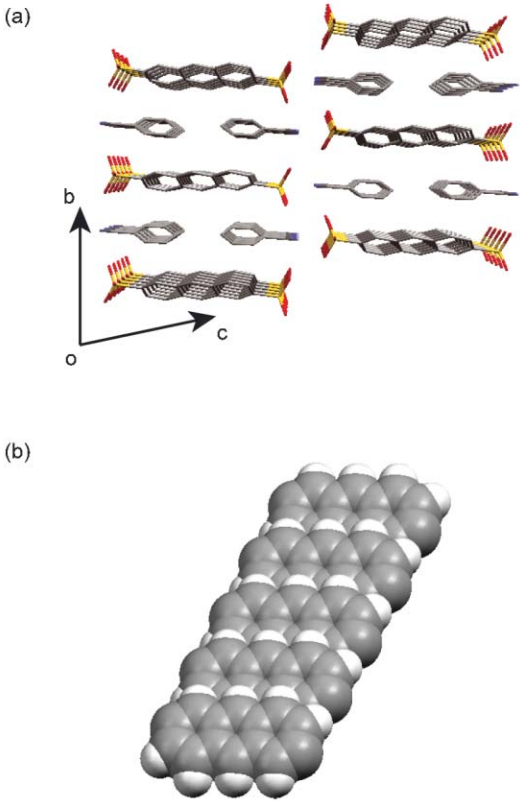

Fig. 1 (a) Packing diagram of crystal structure of **3**; (b) molecular arrangement of anthracene moieties. Hydrogen atoms in (a) are omitted for clarity.

efficiency of **3** exceeded that of the other salts by an order of magnitude. Hence the disposition clearly enhances the fluorescence properties.

To confirm what caused the solid-state emission spectral change, we first compared emission spectra of the organic salts in the solution (Fig. 2 inset). All emission spectra of the salts exhibited the same emission intensity and spectral profile emission band. From this result, the enhancement is shown only in the solid-state. Hence we focus on a T-shaped exciplex between anthracene and benzylamine as the origin of the enhancement only in the solid-state. So far, the T-shaped exciplex between anthracene and toluene has been reported[10] and enhanced the emission intensity.[3] The exciplex generally has no fine vibrational structure.[11,12] In contrast, **3** displays an emission spectrum with fine vibrational structure. Therefore it is most likely that this emission is not due to exciplex fluorescence. This result indicates that the enhancement may not be caused by an electronic factor of benzylamine.

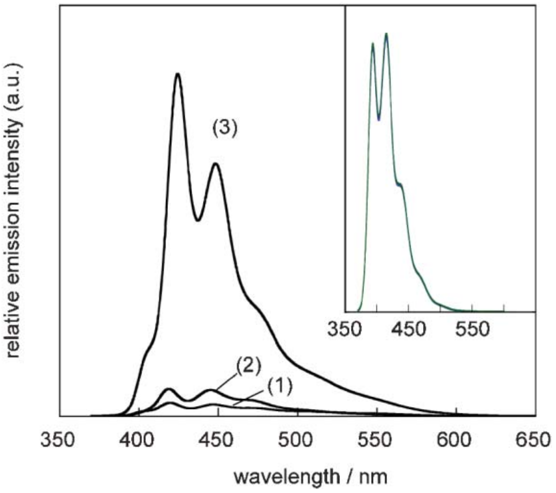

Fig. 2 The solid-state emission spectra of the salts **1–3**. Excitation wavelength was 340 nm in all cases. Inset: the emission spectra of the salts **1–3** in methanol solution. All samples measured in same concentration, 10^{-4} M, and at same excitation wavelength, 340 nm. All spectra overlapped.

Next we hypothesized that a rigid packing in the crystal might be the main cause of the enhancement. In order to prove the hypothesis, we estimated the rigidity of the packing of anthracene moieties in **3**. First, we focus on the packing around the arrangement. From Fig. 3, void spaces between the amines along the *a*-axis in the crystal structure are found to broaden in the following order: **1** < **2** < **3**, and therefore rigidity of the packing should increase in the same order. Secondly, a contraction of the tubulate space was investigated. Tubulate space parameters are defined as the following three-dimensional parameters: interplanar distances between the anthracene rings ($d_{CC(b)}$), interatomic distances between the nitrogen atoms along the *c*-axis ($d_{NN(c)}$) and interatomic distances between the nitrogen atoms along the *a*-axis ($d_{NN(a)}$) as shown in Fig. 4, and the parameters are summarized in Table 2. $d_{CC(b)}$ of **3** became shortened as compared to that of **1** and **2**. The contraction of $d_{CC(b)}$ suggests strong intermolecular interaction between anthracene and the substituent of the amine. Consequently the intermolecular interaction due to the disposition of the benzyl group causes the contraction and the concomitant rigid packing. Lastly, the density of **3** in the crystalline state was higher than that of **1** and **2**. The difference in the density indicates that **3** is more rigid than **1** and **2**.[14] From the above proofs and estimations, the rigidity of the packing increases in the following order: **1** < **2** < **3**, and this order corresponds with the results of the emission quantum efficiency. Therefore the rigidity is the cause of the enhancement due to suppression of the distortion of the anthracene ring and the concomitant nonradiative decay process.[7]

In summary, we have demonstrated that the enhancement was caused by the increase in the rigidity of packing as well. In order to confirm the effect of the rigid packing, the rigid one-dimensional arrangement was prepared by insertion of benzylamines into the tubulate spaces of the host framework consisting of ADS and an amino group. The solid-state fluorescence properties, the crystal structures and the rigidities were evaluated by solid-state emission spectra, quantum efficiency and single X-ray crystallographic study. From these results, strong fluorescence intensity must be provided by not only the decrease in intermolecular interaction but

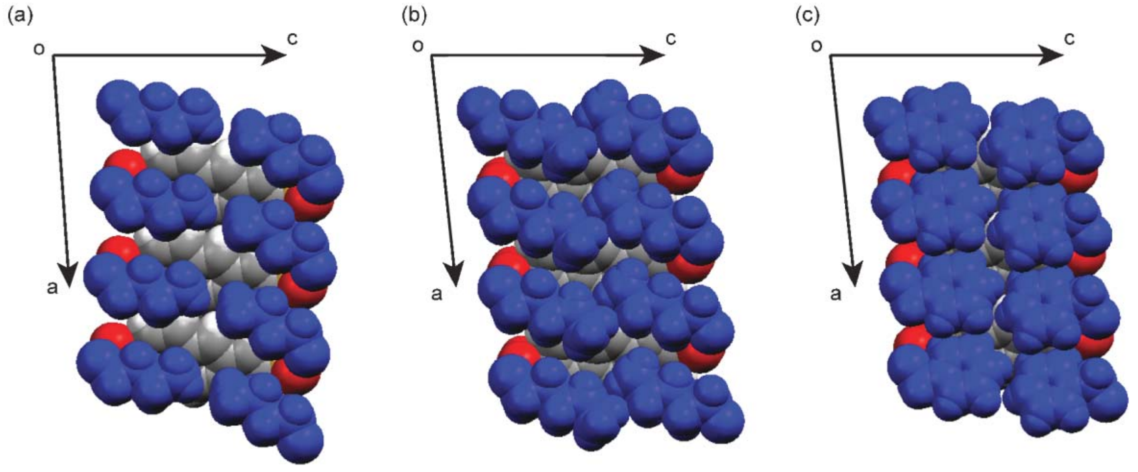

Fig. 3 Molecular packing of (a) **1**, (b) **2** and (c) **3**. Blue molecules represent amines.

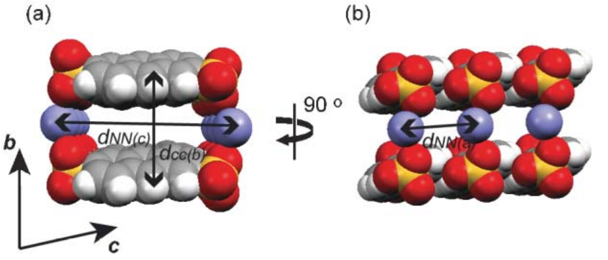

Fig. 4 Tubulate space parameters; interplanar distances between the anthracene rings ($d_{CC(b)}$), interatomic distances between the nitrogen atoms along the *c*-axis ($d_{NN(c)}$) and interatomic distances between the nitrogen atoms along the *a*-axis ($d_{NN(a)}$).

Table 2 The tubulate space parameters of **1**, **2** and **3** and their difference

	Salts		
Parameter	**1**/Å	**2**/Å	**3**/Å
$d_{CC(b)}$	7.390	7.508	7.269
$d_{NN(c)}$	13.473	13.442	13.450
$d_{NN(a)}$	5.650	5.925	5.718

also the increase in the rigidity around the fluorophores. In order to create materials which have the combined features of less intermolecular interactions and more rigidity, screening of the organic salts of ADS with various amines is currently underway in our laboratory.

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Notes and references

† Crystal and analysis data for **1**, $C_{22}H_{32}N_2O_6S_2$; Fw = 484.62; Monoclinic, $P2_1/n$ (#14), Z = 4, a = 5.650(1) Å, b = 14.764(2) Å, c = 29.267(5) Å, β = 94.34(1)°, V = 2434.4(7) Å^3, D = 1.322 g cm^{-3}, μ(CuKα) = 23.19 cm^{-1}, Final R = 0.0843 (Rw = 0.1804) for 3703 observed reflections. Measurements for diffraction data were carried out on a Rigaku RAXIS-RAPID imaging plate diffractometer. The structures were solved by direct methods and refined by a full-matrix least-squares treatment. CCDC 290296. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517687e

‡ Crystal and analysis data for **3**, $C_{14}H_{15}O_2NS$; Fw = 277.34; Triclinic, P-1 (#2), Z = 2, a = 5.7176(8) Å, b = 7.2690(8) Å, c = 14.901(2) Å, α = 78.13(1)°, β = 84.33(1)°, γ = 88.32(1)°, V = 603.0(1) Å^3, D = 1.527 g cm^{-3}, μ(CuKα) = 24.29 cm^{-1}, Final R = 0.0810 (Rw = 0.2420) for 1996 observed reflections. Measurements for diffraction data were carried out on a Rigaku RAXIS-RAPID imaging plate diffractometer. The structures were solved by direct methods and refined by a full-matrix least-squares treatment. CCDC 285636. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517687e

1 A. W. Czarnik, *Acc. Chem. Res.*, 1994, **27**, 302.
2 C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, 1987, **51**, 913; C. W. Tang, S. A. VanSlyke and C. H. Chen, *J. Appl. Phys.*, 1989, **65**, 3610; J. Shi and C. W. Tang, *Appl. Phys. Lett.*, 1997, **70**, 1665.
3 Z. Fei, N. Kocher, C. J. Mohrschladt, H. Ihmels and D. Stalke, *Angew. Chem., Int. Ed.*, 2003, **42**, 783.
4 J. L. Scott, T. Yamada and K. Tanaka, *New J. Chem.*, 2004, **28**, 447; J. L. Scott, T. Yamada and K. Tanaka, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 1697.
5 K. Yoshida, Y. Ooyama, H. Miyazaki and S. Watanabe, *J. Chem. Soc., Perkin Trans. 2*, 2001, 708.
6 Y. Mizobe, N. Tohnai, M. Miyata and Y. Hasegawa, *Chem. Commun.*, 2005, 1839.
7 N. J. Turro, *Modern Molecular Photochemistry*, The Benjamin/Cummings Publishing Company, California, 1978.
8 R. Bishop, *Comprehensive Supramolecular Chemistry, vol. 6 Solid-State Supramolecular Chemistry; Crystal Engineering*, J. L. Atwood, J. E. Davies, D. D. MacNicol and F. Vögtle, Eds; Elsevier, Amsterdam, 1996, p. 85.
9 M. Miyata and K. Sada, *Comprehensive Supramolecular Chemistry, vol. 6 Solid-State Supramolecular Chemistry; Crystal Engineering*, J. L. Atwood, J. E. Davies, D. D. MacNicol and F. Vögtle, Eds; Elsevier, Amsterdam, 1996, p. 147.
10 T. Chakraborty and E. C. Lim, *J. Phys. Chem.*, 1993, **97**, 11151; H. Saigusa and E. C. Lim, *J. Phys. Chem.*, 1995, **99**, 15738.
11 N. Mataga and T. Kubota, *Molecular Interactions and Electronic Spectra*, Marcel Dekker, NewYork, 1970.
12 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley-Interscience, London, 1970.
13 S. Ateş and A. Yilidiz, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 2853.
14 J. D. Dunitz, G. Filippini and A. Gavezzotti, *Tetrahedron*, 2000, **56**, 6595.