

A tunable solid-state fluorescence system consisting of organic salts of anthracene-2,6-disulfonic acid with primary amines†

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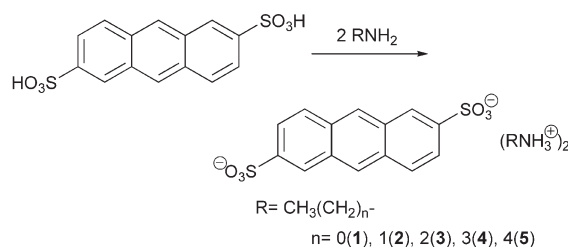
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A dramatic change of solid-state fluorescence properties triggered by molecular arrangements of anthracene moieties was obtained by using organic salts of ADS with primary amines, indicating that modification of the amines enables us to tune the properties.

The development of tunable organic fluorophores has recently met with increasing interest.^{1,2} So far, many approaches have been focused on tuning fluorescence emission properties in solution, such as solvatochromism,³ substituent effects,^{3a,c,4} the alteration of pH^{3a,5} and so on. In particular, the utilization of exogenous additives such as solvent molecules,³ protons^{3a,5} or metal ions^{3a} enables us to modulate the properties readily. In contrast, there are only a few researches about convenient methods of controlling fluorescence emission properties in the solid-state,⁶ which might be more useful for applications such as in electronic and photonic devices.² For example, Stalke and co-workers have found that oxidized diphosphorus-substituted anthracenes exhibit solid-state fluorescence enhancement depending on inclusion of toluene molecules.^{6a} In this communication, we report organic salts of anthracene-2,6-disulfonic acid (ADS) with linear alkylamines as shown in Scheme 1. In addition we estimate a quantitative solid-state fluorescence intensity of the salts by measurement of solid-state fluorescence quantum efficiency (Φ_F). In spite of little difference in the electronic structures of the amines, the solid-state fluorescence emission of these salts was found to depend on the amines as exogenous additives. We propose a tunable solid-state fluorescence system that facilitates the generation of the various properties.



Scheme 1

ADS was prepared according to published procedure.⁷ Organic salts were prepared by mixing ADS and the amines in methanol with a 1 : 2 molar ratio and then by evaporation. The resulting solids were recrystallized from solvents as listed in Table 1 for purification. Salts **1**, **2**, **4** and **5** yielded the corresponding crystals (ADS : amine = 1 : 2) while **3** gave fine powders. The well refined crystals were used for the investigation of the photophysical properties.

Then we measured the fluorescence emission properties of **1**, **2**, **4** and **5** in the solid-state. These crystals show photoluminescence upon illumination with UV light (365 nm) as shown in Fig. 1. **1** and **2** exhibit strong blue emission whereas **4** and **5** exhibit weak emission. To investigate the properties in further detail, we performed the measurements of fluorescence emission spectra and fluorescence quantum efficiencies (Φ_F) in the solid-state. Samples for measurements of the fluorescence emission in the solid-state were prepared under deoxygenated conditions because oxygen molecules can affect the transition fluorescence emission of the salts. The emission quantum efficiencies were determined by standard procedures with an integrating sphere (diameter 6 mm) and quartz cells (diameter 1 mm).⁸ Fig. 2 shows their solid-state fluorescence emission spectra, exhibiting a difference in the spectral profile and a slight shift depending on the alkyl chain length. In the spectra of **1** and **2** (Figs. 2a and b), the band assigned

† Electronic supplementary information (ESI) available: X-ray powder diffraction patterns of **4** and **5**, and FT-IR spectra of **1** and **4**. See <http://www.rsc.org/suppdata/cc/b4/b418241c/>

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Table 1 Experimental, fluorescence spectral and structural data

Salt	Experimental data		Fluorescence spectral data		Structural data	
	Recrystallization solvent	Crystal colour	λ_{em}/nm^b	Φ_F^c	Crystal structure	Arrangement
1	Methanol–water	Colourless	418	0.25	Form I	Two-dimensional
2	Methanol–2-butanone	Colourless	422	0.22	Form I	Two-dimensional
3	N. C. ^a	N. C. ^a	—	—	—	—
4	Methanol–THF	Yellow	419	<0.07	Form II	One-dimensional
5	Methanol–THF	Yellow	417	0.02	Form II	One-dimensional

^a Not crystallized. ^b The wavelength (nm) of the band assigned to $S_0 \rightarrow S_1$ emission. ^c The quantum efficiency determined using anthracene crystal ($\Phi = 0.50$, $\lambda_{em} = 450$ nm) in the solid-state⁸ as the standard.

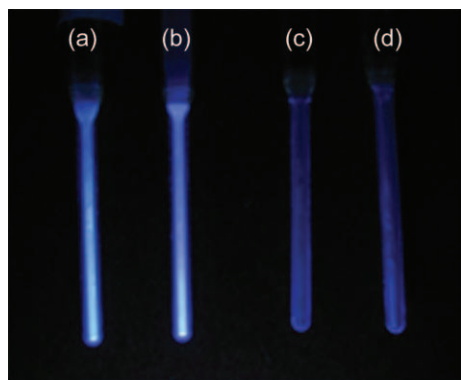


Fig. 1 A snapshot of crystals of (a) **1**, (b) **2**, (c) **4** and (d) **5** in sealed cells. The samples were subjected to UV irradiation.

to the $S_0 \rightarrow S_1$ emission is the highest. On the other hand, those of **4** and **5** (Figs. 2c and d) demonstrate that the band assigned to the $S_0 \rightarrow S_2$ emission becomes higher. Consequently, in the case of **1** and **2**, $S_0 \rightarrow S_1$ emission is the most probable transition. However, the $S_0 \rightarrow S_2$ emission is also effective for the fluorescence properties of **4** and **5**. The spectral data and Φ_F are summarized in Table 1. As compared with wavelength bands, Φ_F dramatically depended on the alkyl chain length. The salts including amines with long alkyl chains exhibit a weak fluorescence, whereas those

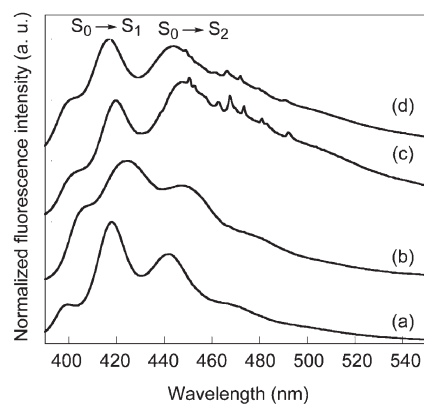


Fig. 2 The solid-state fluorescence emission spectra of crystals of (a) **1**, (b) **2**, (c) **4** and (d) **5** in the solid-state. The excitation wavelength was 340 nm in all cases.

having short alkyl chains exhibit a more than 10-fold higher Φ_F . From the above photophysical results, the fluorescence properties were divided into two types: (i) strong emission for **1** and **2**, and (ii) weak emission for **4** and **5**. These differences in the properties should be caused by the orientation of the anthracene moieties.⁹

In order to elucidate the difference in detail, we carried out X-ray crystallographic analysis of **1**[‡], **2**[§] and **5**[¶]. Inasmuch as **4**

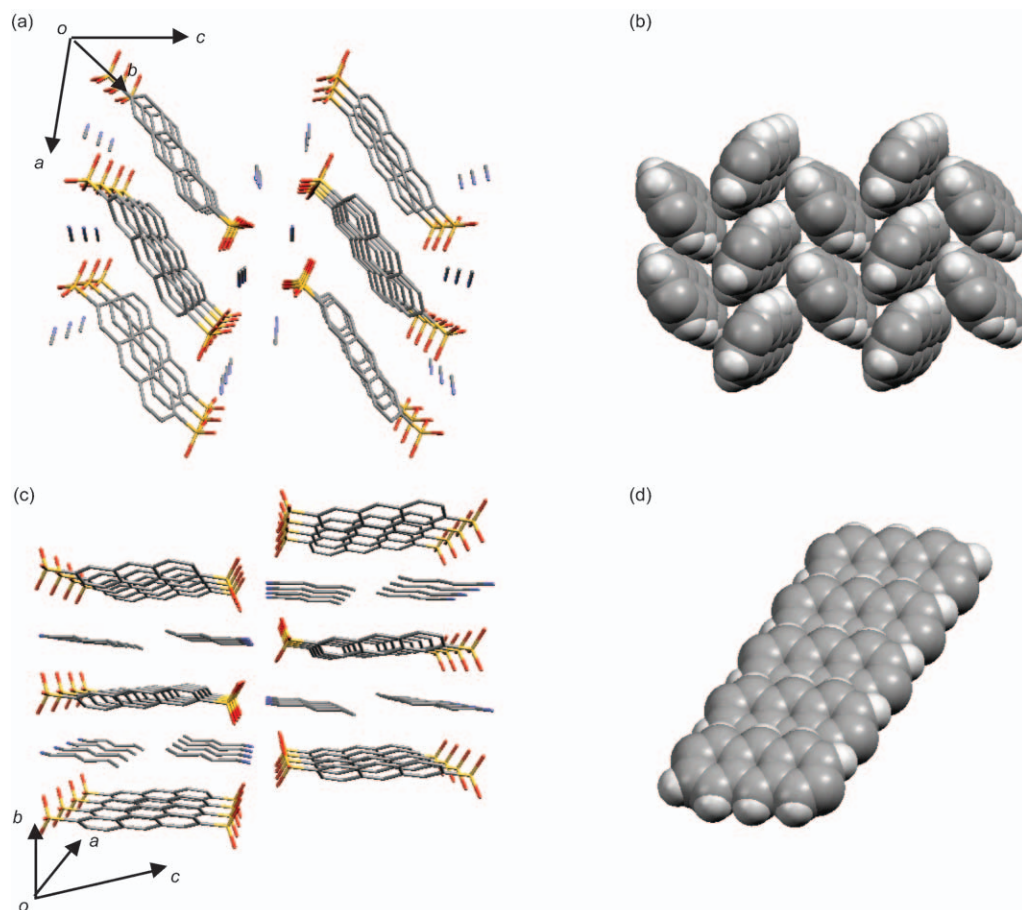


Fig. 3 (a) Crystal structure of **1**[‡]: Form I and (b) two-dimensional arrangement of anthracene moieties. (c) Crystal structure of **5**[¶]: Form II and (d) one-dimensional arrangement of anthracene moieties.

gave thin platelet crystals, the crystal structure of **4** was determined by agreement with the X-ray powder diffraction pattern of **5**.[†] As a result, the crystal structures and corresponding arrangements of the anthracene moieties were also divided into two types: Form I for **1** and **2**, and Form II for **4** and **5**. Those of **1** and **5** are shown in Fig. 3. Form I exhibits a two-dimensional arrangement (Fig. 3 (b)) whereas Form II exhibits a one-dimensional arrangement of anthracene moieties (Fig. 3 (d)).

Further the arrangements are dependent on the alkyl chain lengths of the amines. Fig. 3 (a) demonstrates that Form I is constructed by the alternate stacking of two segregated layers: an amine layer and an ADS layer. On the other hand, Form II is built up by two kinds of columns: an amine column and an ADS column, as shown in Fig. 3 (c). Moreover the alternate stacking of the amine and ADS columns was observed in the direction of the *b*- and *c*-axis. It is likely that the driving forces for the crystallization of these salts are an alkyl chain packing of amines and a π - π stacking of ADS. In other words, the π - π stacking acts as the principal driving force in Form I, whereas the alkyl chain packing also acts in Form II. These differences produce the dramatic change in the arrangements.

The above results suggest that the difference in the fluorescence properties is dependent on interactions inherent to the arrangements. The two-dimensional arrangement in Form I is rigid stacking in comparison with the one-dimensional arrangement in Form II because the two-dimensional arrangement includes more CH- π and π - π interactions than the one-dimensional arrangement. FT-IR spectra of these salts were measured to detect a distortion of the anthracene ring at 1400–1500 cm^{-1} .[†] The distortion in Form I was much smaller than that in Form II. This indicates that many interactions might suppress the distortion and concomitant nonradiative decay process.

Solid-state photophysical properties and functions influenced by the organization of molecules have been attracting interest.^{5,10} Yet, convenient approaches to control the organization and corresponding photophysical properties are rare. The organic salts, composed of ADS and the linear alkylamine, provide a tunable solid-state fluorescence system, where the change in alkyl chain length of amines is translated into the arrangements and corresponding fluorescence properties. The easy synthesis of organic salts and the availability of numerous amines make possible the preparation of diverse arrangements with different properties. In order to create novel properties, such as the spectra shifted to much longer or shorter wavelength, screening of amines such as branched alkyl and aromatic ones is currently underway in our laboratory.

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Notes and references

[†] Crystal data for organic salt of **1**: $\text{C}_8\text{H}_{10}\text{NO}_3\text{S}$, $M = 200.23$, monoclinic, $a = 12.028(9)$, $b = 5.654(4)$, $c = 12.89(1)$ Å, $\beta = 99.20(8)^\circ$, $V = 865(1)$ Å³, $T = 93$ K, space group $P2_1/a$ (no. 14), $Z = 4$, $\mu(\text{Cu}-\text{K}\alpha) = 3.136$ mm^{-1} , $D_c = 1.537$ g cm^{-3} , 7029 reflections measured, 1519 unique ($R_{\text{int}} = 0.077$) which were used in all calculations. The final $R1$ and $wR2$ were 0.059 (observed data) and 0.2224 (observed data), respectively. CCDC 243059.
[‡] Crystal data for organic salt of **2**: $\text{C}_9\text{H}_{12}\text{NO}_3\text{S}$, $M = 214.26$, monoclinic, $a = 35.574(3)$, $b = 7.465(1)$, $c = 7.659(1)$ Å, $\beta = 99.48(1)^\circ$, $V = 2006.3(5)$ Å³, $T = 93$ K, space group $C2/c$ (no. 15), $Z = 8$, $\mu(\text{Cu}-\text{K}\alpha) = 2.741$ mm^{-1} , $D_c = 1.419$ g cm^{-3} , 8504 reflections measured, 1776 unique ($R_{\text{int}} = 0.091$) which were used in all calculations. The final $R1$ and $wR2$ were 0.1064 (observed data) and 0.2950 (observed data), respectively. CCDC 243060.

[¶] Crystal data for organic salt of **5**: $\text{C}_{12}\text{H}_{18}\text{NO}_3\text{S}$, $M = 256.34$, triclinic, $a = 5.925(3)$, $b = 7.508(4)$, $c = 14.947(4)$ Å, $\alpha = 77.02(2)$, $\beta = 82.659(8)$, $\gamma = 86.15(2)^\circ$, $V = 642.1(5)$ Å³, $T = 93$ K, space group $P\bar{1}$ (no. 2), $Z = 2$, $\mu(\text{Cu}-\text{K}\alpha) = 2.226$ mm^{-1} , $D_c = 1.326$ g cm^{-3} , 5190 reflections measured, 2061 unique ($R_{\text{int}} = 0.066$) which were used in all calculations. The final $R1$ and $wR2$ were 0.0749 (observed data) and 0.2412 (observed data), respectively. CCDC 243061. See <http://www.rsc.org/suppdata/cc/b4/b418241c/> for crystallographic data in .cif or other electronic format.

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