PAPER

NJC

www.rsc.org/njc

Guest specific solid-state fluorescence rationalised by reference to solid-state structures and specific intermolecular interactions

Janet L. Scott,*[a] Tomohiko Yamada[b] and Koichi Tanaka[b]

[a] *Centre for Green Chemistry, P.O. Box 23, Monash University, 3800, Victoria, Australia. E-mail: janet.scott@sci.monash.edu.au; Fax: 61 3 9905 4597; Tel: 61 3 9905 4600*

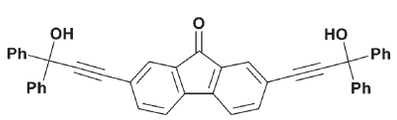
[b] *Department of Applied Chemistry, Faculty of Engineering, Ehime University, Matsuyama, Ehime 790-8577, Japan*

Received* (in Durham, UK) *15th October 2003, Accepted 13th January 2004
First published as an Advance Article on the web 24th February 2004

Guest specific solid-state fluorescence enhancement in 2,7-bis-(3-hydroxy-3,3-diphenylprop-1-ynyl)fluoren-9-one host:guest complexes may be ascribed to changes in the packing modes and hence host–host intermolecular interactions leading to excimer formation in the solid-state and the occurrence (or lack thereof) of specific intermolecular interactions.

Introduction

The phenomenon of fluorescence enhancement in solution upon complexation or binding is frequently used as a means of sensing for specific analytes, but guest specific solid-state luminescence is more rare. Recently, Stalke *et al.* have reported fluorescence enhancement in crystals of disubstituted anthracenes upon toluene complexation[1] and we have noted guest specific effects in the pyridine inclusion complex of 2,7-bis-(3-hydroxy-3,3-diphenylprop-1-ynyl)fluoren-9-one **1**.[2]



1

In somewhat different systems, Ogawa *et al.* report temperature dependent spectral changes, including solid-state fluorescence of salicylideneanilines.[3]

The source of such enhanced emission has been ascribed to packing interactions, but, to the best of our knowledge these have not, in most cases, been elucidated and we now report the genesis of guest specific luminescence enhancement in crystals of **1** with a variety of guest molecules.

Results and discussion

A number of inclusion complexes are formed on recrystallisation of **1** from solution. These complexes range in colour from a very bright acid-yellow to orange and exhibit various host:guest ratios as summarised in Table 1 (absorption spectra of representative complexes reflect these visible changes[2]). While the variation in colour of the host:guest inclusion complexes is easily detected, the difference in emission under UV light is even more striking, as illustrated in Fig. 1 (and reflected in emission spectra[2]).

Crystals of certain complexes luminesce brightly under UV light while others show no enhanced emission.

There appears to be little correlation between the nature of the guest molecule, or the host:guest ratio, and solid-state luminescence. In all cases negligible fluorescence enhancement is observed in solution and solutions of host and guest in a mutual solvent are uniformly bright yellow in colour, in contrast to previously reported chromogenic guest-responsive host compounds, which show solvatochromic effects.[4] Examination of the crystal structures of inclusion complexes of closely related guests, pyridine (exhibiting enhanced solid-state fluorescence) and 3-acetylpyridine (no solid-state fluorescence

Table 1 Selected host:guest complexes of **1**

Guest	H:G ratio	Colour	Luminescent
None	—	light orange	N
Ethyl acetate	1:1	orange	N
THF	1:1	orange yellow	N
Dioxane	1:2	orange yellow	N
Toluene	2:1	orange yellow	N
DMF	1:1	yellow	Y
DMSO	1:2	yellow	some
Pyridine	1:2	acid yellow	Y
3-Acetylpyridine	1:1	orange yellow	N
Triethylamine	1:2	bright yellow	Y
N,N′-Dimethylethylene diamine	2:1	acid yellow	Y
N-Methylpyrolidine	1:2	yellow	Y
N-Methylpiperidine	1:2	yellow	Y

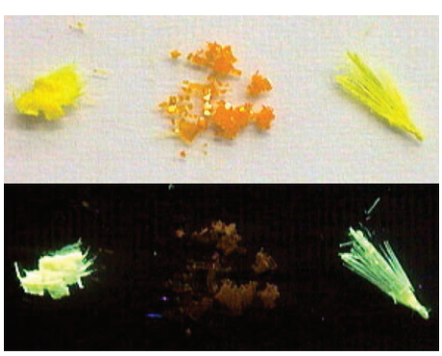


Fig. 1 Crystals of inclusion compounds of **1** under ambient light (top) and UV, 254 nm (bottom). From left: a mass of fine needle-like crystals of **1**·*N,N′*-dimethylethylenediamine, orange rhombs of **1**·ethyl acetate, needles of **1**· 2pyridine grown by slow diffusion of pyridine vapours into a solution of **1** in di-isopropyl ether. The yellow crystals luminesce brightly under UV light.

DOI: 10.1039/b312931d

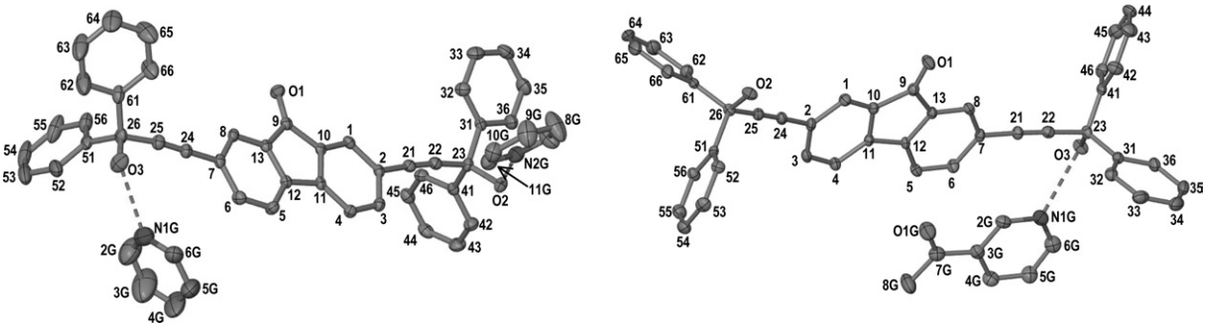


Fig. 2 Molecular diagrams illustrating numbering schemes for **1**·2pyridine (left) and **1**·3-acetylpyridine (right). Hydrogen atoms are omitted for clarity, hydrogen bonds represented by dotted lines and ellipsoids represent the 50% probability level. Greater thermal motion is noted in the terminal phenyl rings and guest pyridine molecules of the **1**·2pyridine complex.

enhancement) reveals some important differences in packing and thus in intermolecular interactions, particularly as these relate to the fluorenone core of host **1**, presumed to be the fluorescent moiety.

Crystal and refinement data and molecular diagrams are presented in Table 2 and Fig. 2.† The complexes of **1** with related guests, pyridine and 3-acetylpyridine, while both crystallising in the common space group $P2_1/c$, exhibit different host:guest ratios and quite dissimilar packing modes.

In **1**·2pyridine guest molecules are hydrogen bonded to the terminal hydroxy groups, as depicted in Fig. 2a, and these host–guest units pack such that stacks, formed of tilted hosts, propagate infinitely along *c*. The fluorenone cores are parallel and exhibit close π···π contacts with interplanar distances of *ca.* 3.4–3.5 Å, as depicted in Fig. 3a. The carbonyl oxygen atoms do not participate in hydrogen-bonding and are sandwiched between aryl rings of the hosts above and below, as depicted in the packing diagram, Fig. 4a. This complex is a bright yellow and exhibits marked fluorescence enhancement, as previously reported.[2]

The inclusion complex **1**·3-acetylpyridine has the guest hydrogen-bonded *via* the pyridine nitrogen to a terminal host hydroxy group (Fig. 2b, Table 3) and pairs of host molecules with close π···π contacts of the fluorenone core but, in sharp contrast to the fluorescent complex, carbonyl groups participate in hydrogen-bonds to one terminal hydroxy group of a neighbouring host (Fig. 4b, Table 3), and π-stacked pairs are bounded by guest molecules (Fig. 3b). This complex shows no fluorescence enhancement in the solid-state. The crystal structure of the previously published **1**·ethyl acetate complex[2] exhibits similar truncated stacks, Fig. 3c, and no luminescence, under UV light, as is evident in Fig. 1.

The luminescence detected in certain of these inclusion complexes is expected to be, as in the case of pure crystalline fluorenone, fluorescence[5] and assuming the fluorenone core to be the moiety responsible for emission it is unlikely that phosphorescence results.[6] If one imagines a crystal as a perfect,

Table 2 Crystal and refinement data for crystalline complexes of **1**

	1·2pyridine	**1**·3-acetylpyridine
Empirical formula	$C_{53}H_{38}N_2O_3$	$C_{50}H_{45}NO_4$
*M*r	750.85	713.79
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	18.3759(4)	16.9301(4)
b/Å	25.4454(8)	8.5045(2)
c/Å	8.7400(2)	25.5885(6)
α/°	90	90
β/°	97.257(2)	92.569(1)
γ/°	90	90
V/Å^3	4053.9(2)	3680.6(2)
Z	4	4
D_c/g.cm^{-3}	1.230	1.288
μ/mm^{-1}	0.076	0.081
Refl. unique	9808	9007
Refl. $I > 2\sigma(I)$	4647	4139
R_1/wR_2 [$I > 2\sigma(I)$]	0.0687/0.1377	0.0606/0.0974
R_1/wR_2 [all data]	0.1746/0.1723	0.1821/0.1266
GoF on F^2	1.028	0.962
paramaters/restraints	531/0	505/0

† CCDC reference numbers 222970 and 222971. See http://www.rsc.org/suppdata/nj/b3/b312931d/ for crystallographic data in .cif or other electronic format.

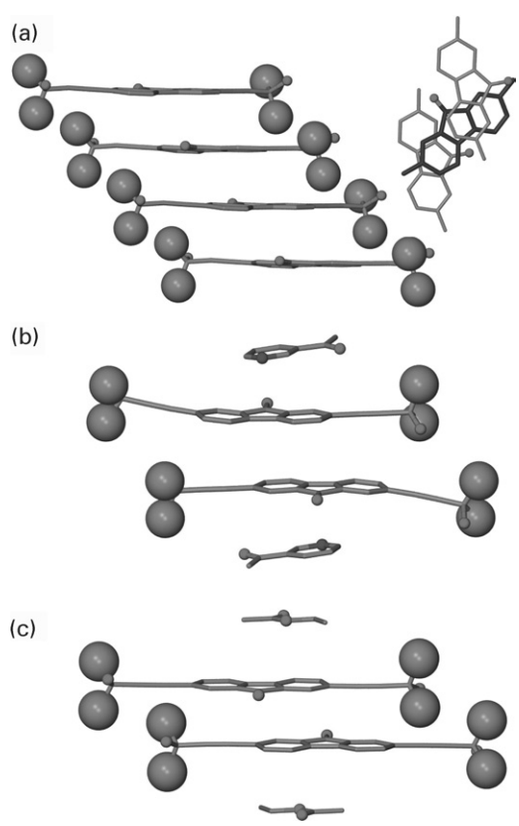


Fig. 3 Molecular stacks in a) **1**·2pyridine, b) **1**·3-acetylpyridine and c) **1**·ethyl acetate (structure previously reported[2]) with terminal phenyl rings replaced by large spheres and heteroatoms represented at 0.2 × van der Waals radius. The fluorescent crystals exhibit continuous stacks of host molecules with overlapping fluorenone moieties (a, overlap illustrated in inset) while the non-fluorescent crystals (b and c) exhibit dimers of hosts which, with guest molecules, form 4 molecule truncated stacks. In all cases the shortest atom to atom distance between the planar fluorenone core of the host molecules is <3.5 Å.

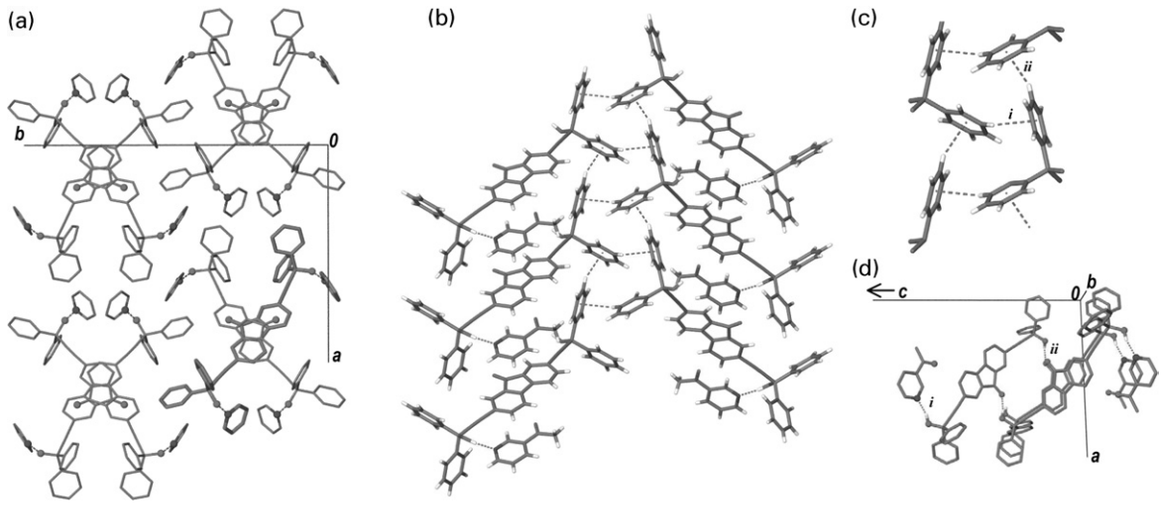


Fig. 4 Packing diagrams a) **1**·2pyridine viewed down [001] (H atoms omitted and one host·2guest unit illustrated with thick lines). Stacks of hydrogen bonded host guest units propagate parallel to *c* and the carbonyl group of the fluorenone core does not participate in hydrogen bonds. A complex network of CH···π interactions exists. b) **1**·3-acetylpyridine viewed perpendicular to (001) with the crossing host–guest–host network omitted to reveal the continuous spiral of CH···π interactions of the terminal phenyl rings of one end of the host (illustrated in close-up in c). c) 'Phenyl embraces' with shared sides forming a continuous spiral//to *c*; *i*) C55–H55$^{(-x,y-\frac{1}{2},\frac{1}{2}-z)}$···centroid (C61–C66), *ii*) C64–H64···centroid (C51–C56)$^{(x,y-1,z)}$. d) Hydrogen bond scheme of **1**·3-acetylpyridine viewed down $-b^*$ with perspective applied; *i*) host–guest H-bond, *ii*) O2–H2O···O1$^{(1-x,y-\frac{1}{2},\frac{1}{2}-z)}$.

'clean' environment (without extraneous quenchers such as dissolved oxygen) then non-radiative decay processes are likely to be mediated by easily examined intra- or intermolecular interactions. The intra- and intermolecular interactions in the crystal may be considered to be the only interactions possible (unless extensive faults occur) and it should be possible to reasonably postulate the source of radiationless decay processes.

The effect of solute–solvent interactions on fluorenone fluorescence have been extensively studied,[7–9] the effect of excimer formation on the position of the emission maximum reported and quenching of fluorescence due to specific interactions between C=O and OH groups, described.[6,10] In the crystalline state, where molecules are held in close proximity to each other (see separation of fluorenone cores), concentration becomes meaningless as all molecules must be in close contact with others and thus excimer formation may be facilitated by a high degree of overlap of planar molecules,[11] leading to P-type delayed emission based on triplet–triplet annihilation processes.[12] While the close registration of pairs of molecules (Fig. 3), and hence increased likelihood of excimer formation, holds for the structures of the non-fluorescing inclusion compounds, the effect of the H-bond (effectively the same as a C=O···H–O–R interaction) or a dipole–dipole interaction,[5] appears to effect radiationless decay of excited states *via* hard cation (alcohol group) and hard anion (excited state carbonyl group) interactions,[13] as described previously for a variety of similar compounds.[14,15] Thus no solid-state fluorescence enhancement is detected in inclusion compounds which have crystal structures that exhibit hydrogen bonds to the carbonyl oxygen while the stacked non-hydrogen bonded pyridine complex shows significant fluorescence enhancement, in the solid, crystalline state, due to excimer formation combined with the lack of close intermolecular which would allow relaxation by non-radiative pathways.

In conclusion: examination of the intermolecular interactions in the single crystal structures of inclusion complexes of **1** thus leads one to the conclusion that, as in solution, existence of a hydrogen bonded complex formed between a hydroxy group and the carbonyl oxygen of the substituted fluorenone, allows for non-radiative decay post excitation, while lack of such intermolecular interaction in the solid-state yields highly fluorescent crystals.

Table 3 Hydrogen bonding geometry

D–H···A	*d*(D–H)/Å	*d*(H···A)/Å	*d*(D···A)/Å	∠DHA/°
1·2pyridine				
O2–H2O···N2G	1.04(3)	1.78(3)	2.823(3)	170(3)
O3–H3O···N1G	1.06(3)	1.70(3)	2.758(3)	175(3)
1·3-acetylpyridine				
O3–H3O···N1G	0.94(3)	1.92(3)	2.818(3)	159(2)
O2–H2O···O1$^{a\,(-x+1,-y+\frac{1}{2},-z+\frac{1}{2})}$	0.89(2)	1.95(3)	2.821(2)	165(2)
1·ethyl acetate				
O2–H2O···O1$^{a\,(-x+1,y+\frac{1}{2},-z-\frac{1}{2})}$	0.94(1)	1.86(2)	2.789(2)	171(2)
O3–H3O···O1G$^{(-x+1,y-\frac{1}{2},-z+\frac{1}{2})}$	0.95(1)	1.92(1)	2.845(2)	164(2)

[a] carbonyl oxygen atom.

Experimental

Inclusion complexes were prepared by recrystallisation of **1** from the relevant solvent. Host:guest ratios were determined by ^{1}H NMR and mass loss on thermogravimetric analysis using a Seiko Instruments TGA/DTA 6200 system.

Crystals suitable for single crystal X-ray diffraction experiments were grown by slow cooling of a solution of **1** in ethyl acetate, by slow evaporation of a solution of **1** with excess 3-acetylpyridine in dichloromethane or by slow diffusion of pyridine vapours into a solution of **1** in di-isopropyl ether. Data were collected on an Enraf-Nonius Kappa CCD diffratometer at 123 K using graphite monochromated Mo–Kα radiation (λ = 0.71073 Å, 1° φ and ω scans). Structures were solved by direct methods using the program SHELXS-97[16] and refined by full matrix least squares refinement on F^2 using the programs SHELXL-97[17] and XSeed.[18] Non-hydrogen atoms of both host and guest were refined anisotropically and hydrogen atoms, except those involved in hydrogen bonding, inserted in geometrically determined positions with temperature factors fixed at 1.2 times (1.5 for methyl hydrogens) that of the parent atom. Hydroxyl group hydrogen atom positions were located

from electron density difference maps and both positional parameters and temperature factors allowed to refine.

References

1 Z. Fei, N. Kocher, C. J. Mohrschladt, H. Ihmels and D. Stalke, *Angew. Chem. Int. Ed.*, 2003, **42**, 783–787.
2 K. Tanaka, M. Asami and J. L. Scott, *J. Chem. Res. (S)*, 2003, 483–484.
3 K. Ogawa, T. Fujiwara and J. Harada, *Mol. Cryst. Liq. Cryst. A*, 2000, **344**, 169–178.
4 K. Tanaka, M. Asami and J. L. Scott, *New J. Chem.*, 2002, **26**, 378–380; J. L. Scott, M. Asami and K. Tanaka, *New J. Chem.*, 2002, **26**, 1822–1826; J. L. Scott, A. P. Downie, M. Asami and K. Tanaka, *CrystEngComm*, 2002, **4**, 580–584.
5 K. Yoshihara and D. R. Kearns, *J. Chem. Phys.*, 1966, **45**, 1991–1999.
6 S. A. Rani, J. Sobhanadri and T. A. P. Rao, *J. Photochem. Photobiol. A*, 1996, **94**, 1–5.
7 L. A. Singer, *Tetrahedron Lett.*, 1969, **12**, 923–926.
8 B. M. Monroe and R. P. Groff, *Tetrahedron Lett.*, 1973, **40**, 3955–3958.
9 T. Kobayashi and S. Nagakura, *Chem. Phys. Lett.*, 1976, **43**, 429–434.
10 L. Biczók, T. Bérces and H. Inoue, *J. Phys. Chem. A*, 1999, **103**, 3837–3842.
11 A. H. Matsui, *Pure Appl. Chem.*, 1995, **67**, 429–436.
12 L. J. Andrews, A. Deroulede and H. Linschitz, *J. Phys. Chem.*, 1978, **82**, 2304–2309.
13 A. Morimoito, T. Yatsuhashi, T. Shimada, L. Biczók, D. A. Tryk and H. Inoue, *J. Phys. Chem. A*, 2001, **105**, 10 488–10 496.
14 H. Inoue, M. Hida, N. Nakashima and K. Yoshihara, *J. Phys. Chem.*, 1982, **86**, 3184–3188.
15 H. Saigusa and E. C. Lim, *J. Phys. Chem.*, 1995, **99**, 15 738–15 747.
16 G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997.
17 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.
18 L. J. Barbour, *J. Supramol. Chem.*, 2001, **1**, 189.