On the Mechanism of Matrix-Assisted Room Temperature Phosphorescence

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Our recent studies[1] of the photophysical properties of dye inclusion crystals (DICs), transparent crystals that contain oriented, isolated organic chromophores, have led to a new understanding, described herein, of solid surface room temperature phosphorescence (SSRTP), a simple method for detecting drugs, pollutants, polymers, and biomolecules that have been deposited on various solid surfaces.[2] Despite the growth of SSRTP as a method of analysis, knowledge of the requisite physicochemical interactions between phosphors and substrates that obviate collisional deactivation of triplet excited states at relatively high temperatures is incomplete. The chromophore and surface combinations that will produce measurable phosphorescence quantum efficiencies cannot be predicted.[3] Since we have often observed room temperature phosphorescence (RTP) from DICs, we set out to characterize the long-lived luminescence from these crystals with the expectation that such a program of research might illuminate mechanisms of SSRTP. Herein, we report the detailed characterization of one DIC that phosphoresces at room temperature, 2-aminonaphthalene-1,5-disulfonate (ANDS) in K_2SO_4, and show how an analogous treatment of *p*-aminobenzoic acid (PABA) solutions applied to sodium acetate (NaOAc) powders, the most well-studied SSRTP system, specifies the chemical interactions that give rise to RTP. With judgments about mixed crystal growth drawn from these examples we were then able to select a new RTP matrix, $Ba(OAc)_2$, with improved efficiency and predictable optical properties.

K_2SO_4 crystals (*Pmcn*)[4] with luminescent {021} growth sectors were grown at room temperature by the evaporation of saturated aqueous salt solutions containing ANDS (7.0×10^{-4} M) (Figure 1a). The average molar ratio of K_2SO_4 to ANDS in dyed growth sectors was (5.0×10^4):1. We measured, at room temperature, the energies and polarizations of the excitation[5] ($\lambda_{ex} = 350$ nm), fluorescence ($\lambda_f = 420$ nm), and phosphorescence ($\lambda_p = 520$ nm), the lifetimes of the luminescence ($\tau_f = 5.0$ ns, $\tau_p = 0.7$ s), and the triplet excited state **g** ($|g_X| = 2.001(3)$, $|g_Y| = 1.998(3)$, $|g_Z| = 1.995(3)$), and **D** ($|D_X| = 0.0424(2)$, $|D_Y| = 0.0018(2)$, $|D_Z| = 0.0442(2)\text{cm}^{-1}$; $D = 0.0663$ cm^{-1}; $E = 0.0203$ cm^{-1}) tensors.[6] The D value, considerably smaller than that in naphthalene (0.1003 cm^{-1}),[7] is consistent with a conformation in which the $-NH_2$ group lone pair is in conjugation with the π system, making one H···O−S contact with the adjacent $-SO_3^-$ group. In conjunction with calculations of the electronic transition dipole moments (ETDM) using INDO/S-CI[8] and the **D**-tensor using a weighted point charge approximation,[9] we determined the orientation of ANDS with respect to the crystallographic axes; unit vectors corresponding to the calculated ETDM and **D** tensor eigenvectors were least-squares fit to the corresponding experimentally determined vectors. The angle between the calculated and experimental ETDMs was 8.9°, and those between the D_X, D_Y, and D_Z tensor elements were 4.1, 1.9, and 4.2°, respectively. ANDS in this orientation disposes the S−C vector of the 1-SO_3^- substituent 10.6° from an S−O bond emerging from the {021} surface, suggestive of a recognition mechanism in which the substitution of a sulfonate group for a sulfate ion on these surfaces orients the ANDS molecules within the lattice;[10] subsequent entrapment thereby produces RTP due to the obviation of collisional deactivation in the salt "tomb"[11,12] (Figure 2).

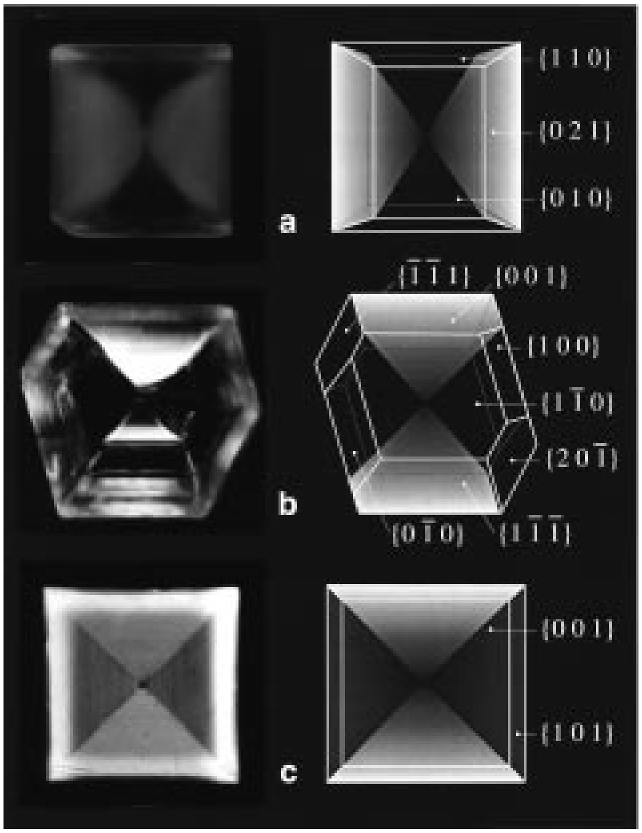

Figure 1. Photographs of RTP from crystals illuminated with polarized UV light with idealized representations of their habits: (a) K_2SO_4/ANDS (2 mm × 2 mm × 1 mm), (b) $NaOAc{\bullet}3H_2O/PAB^-$ (13 mm × 12 mm × 3 mm), (c) $Ba(OAc)_2/PAB^-$ (8 mm × 8 mm × 2 mm). Edges of crystals are illuminated due to reflected light.

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(1) Kahr, B.; Jang S−H.; Subramony J. A.; Kelley M. P., Bastin, L. *Adv. Mater.* **1996**, *8*, 941−944 and references therein.

(2) Vo-Dinh, T. *Room-Temperature Phosphorimetry for Chemical Analysis: Theory, Instrumentation, and Applications*; Marcel Dekker: New York, 1981. Hurtubise, R. J. *Phosphorimetry: Theory, Instrumentaion and Applications*, VCH: New York, 1990.

(3) (a) Gunshefski, M.; Santana, J. J.; Stephenson, J.; Winefordner, J. D. *Appl. Spectrosc. Rev.* **1992**, *27*, 143−192. (b) Hurtubise, R. J. *Anal. Chim. Acta* **1997**, *351*, 1−22.

(4) Ojima, K.; Nishihata, Y.; Sawada, A. *Acta Crystallogr. Sect. B* **1995**, *B51*, 287−293.

(5) Fluorescence emission and excitation spectra were collected as reported previously (Chmielewski, J.; Lewis, J. J.; Lovell, S.; Zutshi, R.; Savickas, P.; Mitchell, C. A.; Subramony, J. A.; Kahr, B. *J. Am. Chem. Soc.* **1997**, *119*, 10565−10566) using a SPEX Fluormax fluorometer that was coupled to a polarizing microscope when the excitation energies were in the visible part of the spectrum. Phosphorescence spectra were collected using a homemade rotating can phosphoroscope. Fluorescence and phosphorescence lifetimes were recorded on a PTI LaserStrobe Timemaster fluorescence lifetime spectrometer with a phosphorescence accessory. EPR spectra were collected on a Bruker ESP 300 EPR spectrometer (X band) with a 100 kHz modulation. Crystals in the EPR experiments were irradiated with an Oriel mercury−xenon arc lamp operating at 200 W equipped with a water filter and a Corning #C50-56 long pass filter (>260 nm).

(6) Weil, J. A. *EPR-NMR*, 1993.

(7) Hutichson, C. A.; Magnum, B. W. *J. Chem. Phys.* **1961**, *34*, 908−922.

(8) Ridley, J.; Zerner, M. C. *Theor. Chim. Acta* **1973**, *32*, 111−134; **1976**, *42*, 223−236.

(9) Hilinski, E. F. Ph. D. dissertation, Yale University, 1986.

(10) Kelley, M. P.; Janssens, B.; Vetter, W.; Kahr, B. *J. Am. Chem. Soc.* **1994**, *116*, 5519−5520. Rifani, M.; Yin, Y.; Elliott, D.; Jay, M. J.; Jang, S.-H.; Kelley, M. P.; Bastin, L.; Kahr, B. *J. Am. Chem. Soc.* **1995**, *117*, 7572−7573. Kahr, B.; Kelley, M. P. In *Supramolecular Stereochemistry*; Siegel, J. S., ed.; NATO ASI Series, Kluwer: Dortrecht, 1995; pp 203−227.

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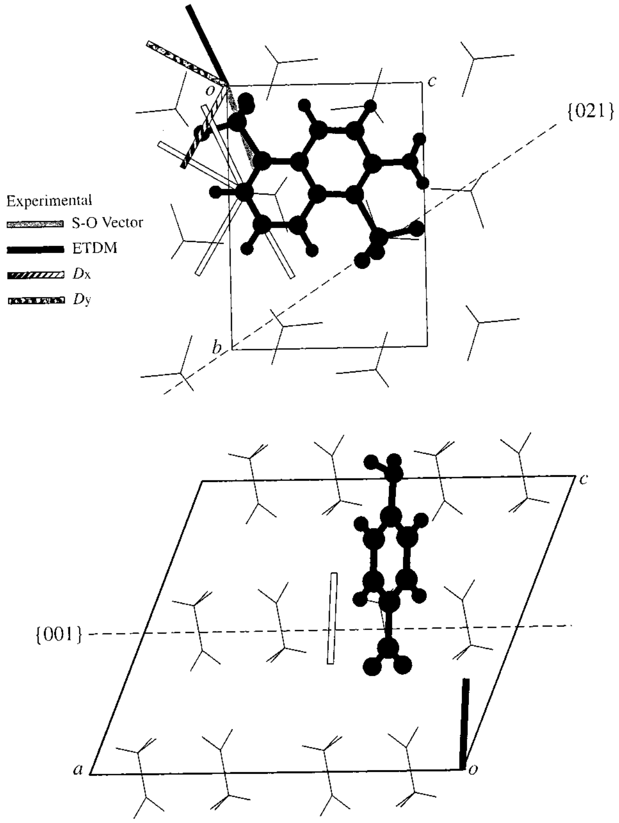

Figure 2. Structure of mixed crystals. Colorless vectors represent calculated quantities for molecules. (Top) K_2SO_4/ANDS. K^+ ions have been omitted for clarity. (Bottom) $NaOAc{\cdot}3H_2O/PAB^-$. Na^+ ions and H_2O molecules have been omitted for clarity.

PABA solutions deposited on NaOAc and other solid matrixes have been studied since 1976 by Hurtubise and co-workers.[13] Initially they presumed that *p*-aminobenzoate (PAB^-) was hydrogen-bound to NaOAc surfaces but by 1990 incisively deduced from the linear relation between heat capacity and radiationless phosphorescence decay that PAB^- was inside the lattice.[14] But the direct observation of the phosphorescence from PAB^- or any luminophore within single crystals of NaOAc or of any other host has not been illustrated despite earlier efforts.[13a]

Our discovery that RTP is a common attribute of DICs and the observations of Hurtubise and co-workers are consistent with a SSRTP (now preferably called MARTP, matrix-assisted room temperature phosphorescence) mechanism whereby the matrix is dissolved by protic solvents (evaporated H_2O and EtOH solutions give RTP but ether and acetone solutions do not), and microcrystals reform during evaporation, orienting and isolating the phosphors.[15] Therefore, we were emboldened to try to prepare large single crystals of $NaOAc/PAB^-$ as we had done for K_2SO_4/ANDS in hopes of demonstrating MARTP directly so that we could deduce a mechanism for mixed crystal growth from the anisotropy of the optical properties.

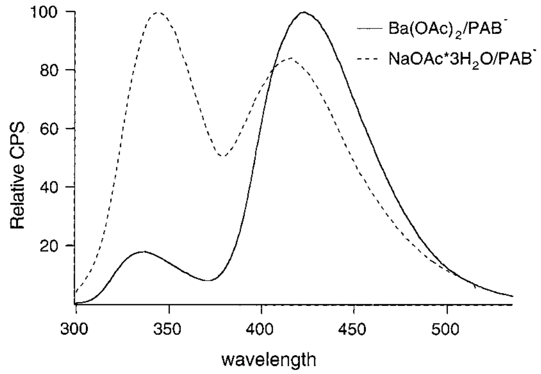

Figure 3. Luminescence spectra of $NaOAc{\cdot}3H_2O/PAB^-$ and $Ba(OAc)_2/PAB^-$ mixed crystals. The short and long wavelength emissions correspond to room temperature fluorescence and phosphorescence, respectively.

$NaOAc{\cdot}3H_2O$ crystals ($C2/c$)[16] with luminescent {001} growth sectors were grown at room temperature from saturated aqueous salt solutions containing PABA (0.19 M) (Figure 1b). The average ratio of moles of NaOAc to moles of PABA in these crystals is (1.7×10^3):1. The energies ($\lambda_{ex} = 286$ nm, $\lambda_f = 344$ nm, $\lambda_p = 413$ nm), lifetimes ($\tau_f = 2.2$ ns, $\tau_p = 1.6$ s), and relative intensities of the phosphorescence and fluorescence of $NaOAc{\cdot}3H_2O/PAB^-$ crystals compare favorably with those quantities from dehydrated mixed crystals measured in our labs and from PABA deposited on anhydrous NaOAc powders, reported previously.[13]

The long axis transition moment[17] of PAB^- included within the $NaOAc{\cdot}3H_2O$ crystal was determined from the luminescence intensity as a function of excitation polarization with light incident on {110} and {010}; it was found to be perpendicular to {001}, consistent with PAB^- approaching the surface carboxylate first and substituting in the place of an acetate ion carboxylate group (Figure 2). The misalignment of the host and guest $C-COO^-$ vectors in this model is 12.3°.

Given these chemically sensible sulfate–sulfonate and carboxylate–carboxylate substitution models, we selected a crystalline matrix for RTP that would orient PAB^- predictably and promote phosphorescence via heavy atom induced spin–orbit coupling.[18] Tetragonal ($I4_1/a$)[19] $Ba(OAc)_2$ crystals grown from PAB^- solutions contained the guest in the {101} growth sectors. The luminescence, almost exclusively phosphorescence ($\lambda_p = 427$ nm, Figure 3) with a predictably shorter lifetime ($\tau_p = 5.4$ ms) than that of $NaOAc{\cdot}3H_2O/PAB^-$ crystals due to rapid intersystem crossing, was polarized orthogonally in adjacent sectors according to the host symmetry and is consistent with a carboxylate–carboxylate substitution model involving acetate ions emergent from the {101} faces. Comparisons of a variety of phosphorescent guests in single crystals of K_2SO_4, $NaOAc{\cdot}3H_2O$, and $Ba(OAc)_2$ will be forthcoming.

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[11] Kirkor, E.; Gebicki, J.; Phillips, D. R.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 7106–7107.

[12] The 5-SO_3^- subtituent is unnecessary, a judgment supported by the fact that the optical and magnetic anisotropies of ANDS and 2-aminonaphthalene-1-sulfonate in K_2SO_4 are equivalent.

[13] (a) von Wandruszka, R. M. A.; Hurtubise, R. J. *Anal. Chem.* **1976**, *48*, 1784–1788. (b) von Wandruszka, R. M. A.; Hurtubise, R. J. *Anal. Chem.* **1977**, *49*, 2164–2169.

[14] Ramasamy, V. P.; Hurtubise, R. J. *Anal. Chem.* **1990**, *62*, 1060–1064. Ramasamy, V. P.; Hurtubise, R. J. *Appl. Spectrosc.* **1990**, *44*, 1494–1497. Hurtubise, R. J.; Ramasamy, V. P.; Boerio-Goates, J.; Putnam, R. *J. Lumin.* **1996**, *55–68.*

[15] Matrix isolation mechanisms in RTP due to swelling and shrinking of cellulose fibers and by "packing" cellulose with added salts and sugars have been proposed previously. See: Niday, G. J.; Seybold, P. G. *Anal. Chem.* **1978**, *50*, 1577–1578. McAleese, D. L.; Dunlap, R. B. *Anal. Chem.* **1984**, *56*, 2244–2246.

[16] Efremov, V. A.; Endeladze, N. O.; Agre, V. M.; Trunov, V. K. *Zh. Strukt. Khim.* **1986**, *27*, 177–180.

[17] Halpern, A. M.; Ramachandran, B. R. *Photochem. Photobiol.* **1995**, *62*, 686–691.

[18] Seybold, P. G.; White, W. *Anal. Chem.* **1975**, *47*, 1199–1200. White, W.; Seybold, P. G. *J. Phys. Chem.* **1977**, *81*, 2035–2040.

[19] Gautier-Luneau, I.; Mosset, A. *J. Solid State Chem.* **1988**, *73*, 473–479.