Room-Temperature Phosphorescence of Amorphous Metal Complexes of Aliphatic Carboxylic Acids with Basic Amino Acids

Richard S. Turk,* Joel I. Dulebohn, and DeLynne Vail

Michigan Biotechnology Institute, PO Box 27609, Lansing, Michigan 48909

Received September 19, 1994. Revised Manuscript Received December 6, 1994[⊗]

Luminescent materials have been prepared from aqueous gels of metal salts of dicarboxylic and some monocarboxylic acids with the basic amino acid lysine and its related amino acids ornithine and diaminopimelic acid. The development of an amorphous structure is required for room-temperature phosphorescence in the solid and is dependent on various factors including stoichiometry, metal type, and the size of the organic acid. Studies with commercial grades of lysine prepared from various sources and magnesium oxide or zinc oxide as the metal oxide indicate that linear aliphatic dicarboxylic acids of three to six carbons in length produce maximal emission. For a given chain length the photoluminescence intensity decreases with cation radius according to Li > Na > K for alkali metals and Mg > Ca > Sr > Ba for alkaline-earth metals. Development of intense fluorescence and phosphorescence emission correlates to noncrystalline structures, and based on the given method of preparation, phosphorescence was not obtained with crystalline products. The simple and rapid preparation of this new biological glass provides a matrix for the further investigation of the photophysics of organic compounds of biological interest and their interactions with different molecular environments.

Introduction

Amorphous substances, formed either from cooling viscous melts or from liquids after transition from sol to gel, provide a rigid molecular environment necessary to induce phosphorescence in the solid state. Oxide glasses, generally the silicates, are familiar amorphous solids that can be fabricated into optically transparent materials in which to study molecular luminescence phenomena.[1-3] The most investigated sol–gel glasses are those prepared from the hydrolysis and polymerization of metal alkoxides. The typical composition of sol–gel glasses comprises metal oxides from group IV elements (Ti, Si, Ge). Recently the observation of room-temperature phosphorescence from trapped organic molecules in a porous silica matrix prepared by sol–gel polymerization has been reported.[4]

The phenomena of room-temperature fluorescence and phosphorescence are observed from several aromatic organic molecules adsorbed or trapped in solid matrices.[5-7] Various organic materials have been used to enhance molecular luminescence in the solid state. Spectroscopic studies of the electronic states of rare-earth metals and trace organic compounds have been described for molecules trapped in organic cryptands, β-cyclodextrin, and polymeric matrices.[8-10] Organic acids and organic acid polymeric materials such as sodium acetate and polyacrylic acid are used to promote long-lifetime room-temperature phosphorescence from aromatic organic anions adsorbed on surfaces.[11,12]

Several large-scale fermentation processes are now available for production of basic biochemical materials such as amino acids and organic acids.[13] Fermentation technologies can potentially produce biomolecular materials which have specially designed chemical, electronic, optical, and structural properties using biological or natural sources.[14] The combination of sol–gel processes with biological systems has been utilized to make novel composite materials including nanometer-sized magnetite particles and semiconductor–glass composites exhibiting quantum confinement effects.[3] Biomolecular materials having similar optical properties to amorphous and crystalline inorganic semiconductors could be useful for developing new photoactive devices such as biological photodetectors and molecular sensors.

This paper begins to explore the stability of long-lived excited electronic states of complex materials of biological interest. Studies of the molecular interactions and aggregations of amino acids and amino acid complexes with succinic acid have elucidated noncovalent interactions that play a role in the assembly of biomolecules.[15,16] Metal ions Mg^{2+}, Zn^{2+}, and Ca^{2+} have important associations with amino and carboxylic acids in

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1995.

(1) Kaufman, V. R.; Levy, D.; Avnir, D. *J. Non-Cryst. Solids* **1986,** *82,* 103.
(2) Reisfeld, R. *J. Non-Cryst. Solids* **1990,** *121,* 254.
(3) Ulrich, D. R. *J. Non-Cryst. Solids* **1990,** *121,* 465.
(4) Levy, D.; Avnir, D. *J. Photochem. Photobiol A: Chem.* **1991,** *57,* 41.
(5) Hurtubise, R. J.; Ramasamy, S. M. *J. Lumin.* **1994,** *59,* 147.
(6) Hurtubise, R. J. *Phosphorimetry: Theory, Instrumentation, and Applications*; VCH: New York, 1990.
(7) Vo-Dinh, T. *Room Temperature Phosphorimetry for Chemical Analysis*; Wiley: New York, 1984.
(8) Bredol, M. U.; Kynast, M.; Ronda, C. *Adv. Mater. J.* **1991,** *7/8,* 361.
(9) Jones, P. F.; Siegel, S. *J. Chem. Phys.* **1969,** *50,* 1134.
(10) Corly, J. S.; Hurtubise, R. J. *Appl. Spectrosc.* **1994,** *48,* 747.
(11) Senthilnathan, V. P.; Hurtubise, R. J. *Anal. Chem.* **1985,** *57,* 1227.
(12) Dalterio, R. A.; Hurtubise, R. J. *Anal. Chem.* **1983,** *55,* 1084.
(13) Moo-Young, M.; Ed.; *Comprehensive Biotechnology*; Pergamon Press: Oxford, 1985; Vol. III.
(14) Freedman, D. H. *Science* **1991,** *254,* 1308.

0897-4756/95/2807-0385$09.00/0

many biological processes such as enzyme catalysis, photosynthesis, and stabilization of protein and nucleic acid structures.[17] Both group I and II metal ions are known to coordinate with various dicarboxylic acids; alkaline-earth-metal coordination compounds can also be formed with dibasic amino acids.[18] Although long-lived excited states leading to phosphorescence are usually associated with the solid state at low temperature, intrinsic phosphorescence of proteins in solution at room temperature can be detected from samples in which the quenching by molecular oxygen is reduced.[19] Ideally, detection of intrinsic phosphorescence of amino acids and proteins and study of their interaction with other molecules would also be possible in the solid state if these molecules could be trapped in a water-soluble solid matrix with low permeability to oxygen. Room-temperature phosphorescence of biochemically important molecules adsorbed on solid matrices has been enhanced in materials containing heavy cations and anions.[20] Aromatic amino acids (tyrosine and tryptophan) and derivatives show enhanced luminescence when adsorbed on porous supports such as cellulose impregnated with sodium iodide.[21] Although the spectroscopic properties of ions in acetate glasses have been studied,[22,23] the use of group I and group II cation coordination complexes of naturally occurring amino acids with organic acids for the enhancement of photoluminescence has not been previously reported.

The inorganic metal salts used in this study are known to form photoluminescent materials (phosphors) under high-temperature and nonaqueous environments. Several natural minerals (calcite, $CaCO_3$; magnesite, $MgCO_3$; gypsum, $CaSO_4 \cdot H_2O$; lime, CaO; periclase, MgO; fluorapatite, $Ca_5(PO_4)_3F$) are composed of group II elements and may contain substitutional impurities or point defects which give them phosphorescent and fluorescent properties.[24-26] Alkali and alkaline-earth silicate glasses containing rare-earth metals also exhibit luminescence which is dependent on the presence of oxides of group I and group II metals.[27] This property has application in the preparation of solid-state laser glasses.[28] In general, interaction of these minerals with water-soluble organic acids destroys their natural luminescence due to irreversible dissolution and hydration of their crystal lattice structure.

In this work, metal complexes of several small monocarboxylic acids and aliphatic dicarboxylic acids in combination with the basic amino acids lysine and diaminopimelic acid have been fabricated into optically transparent amorphous materials that promote intense room-temperature phosphorescence and fluorescence. The complexation of group II metals with the organic salt of lysine and selected carboxylic acids enhances the efficiency of an intrinsic phosphorescence which requires the development of the glassy state. Room-temperature phosphorescence of the glass matrices is quenched by the presence of excess water in these hydroscopic materials but does not appear to be effected by the diffusion of oxygen. Thermal processing of these materials to evaporate excess water removes the quenching process and full luminescence is recovered.

Experimental Section

Preparation of Metal Complexes. Several commercial sources of L-lysine, DL-lysine, D-lysine, and L-lysine monohydrate can be used. These materials are prepared by various fermentation processes from different starting materials or by chemical synthesis. L-Lysine monohydrate (Degussa Corp., >98.5% purity) was used as the primary source from fermentation as supplied. DL-Lysine (50% aqueous) from Fluka and D-lysine (Sigma) are synthetic materials. L-Lysine hydrate, L-lysine (Aldrich), and L-lysine (Sigma) were alternate sources of fermentation grade lysine (>98% purity). The general method for production of the phosphor involves dissolving 0.061 mol (10 g of lysine monohydrate) in 6 mL of water at 60−70 °C and adding 0.061 mol of reagent-grade metal oxide (MgO, CaO, SrO, Li_2O, BeO, ZnO, BaO) to form a slurry. The corresponding carboxylic acid (succinic acid is the model compound) is added, and an exothermic heat of reaction to form the dissolved metal complex is observed. The temperature increases to 100 °C, and in several cases a thick, clear gel is formed.

The dissolution of the metal ion [M] occurs by the following reaction scheme:

1. Dissolution with organic acid [A], $n = 1, 2$:

$$M_{2/n}O + H_2A \rightarrow (2/n)M[H_2O]^{n+} + A^{2-}$$

2. Complexation of the neutral amino acid [L]

to form a gel:

$$(2/n)M[H_2O]^{n+} + L \rightarrow M_{2/n}L[H_2O]_{2/n}{}^{n+}$$

The enhanced water solubility of the metal salts in the presence of amino acid suggest this coordination scheme. At 40 °C calcium succinate has a solubility of <1 g %, but in the amino gel the solubility increases to >35 g %.

The gel is dried in a conventional microwave oven for 1−5 min. In some thermally unstable formulations the material is removed just prior to burning. Alternatively, gels are dried in a conventional oven at 120 °C for 1 h. The solid is cooled by placing in a freezer (−5 °C) for 10 min and then brought to room temperature for evaluation. Hydroscopic materials are stored in sealed glass vials.

Instrumentation. Excitation and emission spectra were carried out on an SLM-Aminco Bowmen Series 2 luminescence spectrometer. Samples were placed on a front surface adapter. Intensity and lifetime measurements were performed on a benchtop light meter. A mineral lamp (Spectronics Corp., Westbury, NY) source is used to excite the sample at 365 nm which is mounted in a glass well (1.25 in. diameter (0.008 522 ft^2)) on a Polaroid FP-4 shutter. The shutter is placed over a selenium photovoltaic cell attached to a YFE Digital Light Meter (Mitchell Instruments, San Marcos, CA). The output in foot-candles (fc = lumen/ft^2) is recorded on a linear chart recorder with a response factor of 0.1 fc/cm. Minimum detection of the phosphorescence is 0.01 fc. Lifetimes (t, seconds) were calculated from a single-component exponential curve and are reported as the time required to decay 36.8% of

(15) Vijayan, M. *Prog. Biophys. Mol. Biol.* **1988**, *52*, 71.
(16) Prasad, G. S.; Vijayan, M. *Biopolymers* **1993**, *33*, 283.
(17) Sigel, H.; Martin, R. B. *Chem. Soc. Rev.* **1994**, 83.
(18) Schmidbauer, H.; Classen, H. G.; Helbig, J. *Angew. Chem., Int. Ed. Eng.* **1990**, *29*, 1090.
(19) Vanderkooi, J. M.; Calhoun, D. B.; Englander, S. W. *Science* **1987**, *236*, 568.
(20) Aaron, J. J.; Campiglia, A. D.; Winefordner, J. D. *Anal. Chim. Acta* **1990**, *236*, 257.
(21) Meyer, M. L.; Seybold, P. G. *Anal. Chem.* **1979**, *51*, 1609.
(22) Duffy, J. A.; Ingram, M. D. *J. Chem. Soc. A* **1969**, 2398.
(23) Ingram, M. D.; Lewis, G. G.; Duffy, J. A. *J. Phys. Chem.* **1972**, *76*, 1035.
(24) Baldacchini, G., Di Bartolo, B., Ed.; *Optical Properties of Excited States in Solids*; Plenum Press: New York, 1992.
(25) Abramishvili, M. G.; Akhvlediani, Z. G.; Kalabegishvili, T. L.; Kvachadzi, V. G. *Phys. Status Solidi B* **1993**, *175*, 77.
(26) Leverenz, H. W. *An Introduction to Luminescence of Solids*; Dover Publications: New York, 1968.
(27) Nageno, Y.; Takebe, H.; Moringa, K.; Izumitani, T. *J. Non-Cryst. Solids* **1994**, *169*, 288.
(28) Patek, K. *Glass Lasers*; Butterworth: London, 1970.

Table 1. Phosphorescence of Lysine Succinate Salts Prepared from Metal Ions from Various Periodic Groups

	group metal[a] (charge)	ionic radius[b] (pm)	rel intensity[c]
IA	Li(+1)	68	0.5
IA	Na(+1)	97	0.2
IA	K(+1)	133	0.05
IIA	Be(+2)	35	0.1
IIA	Mg(+2)	66	1.0
IIA	Ca(+2)	99	0.2
IIA	Sr(+2)	112	0.1
IIA	Ba(+2)	135	0.0
IIB	Zn(+2)	74	1.5
IIIA	Al(+3)	51	0.0
IVA	Si(+4)	42	0.05

[a] Metal oxides were used to prepare Li, Be, Mg, Ca, Al, and Zn salts. Hydroxides were used for K, Na, carbonate for Sr and silicic acid for Si. Hydroxides and carbonates of Mg, Zn, and Ca can be used with similar results. [b] Ionic radii from: *CRC Handbook of Chemistry and Physics*, 61st ed.; 1980–81. [c] Phosphorescence measured after excitation with a mineral lamp at 365 nm. The relative intensity of phosphorescence is $[Q/Q_{Mg}]$, where Q_{Mg} is the intensity of the magnesium salt.

its initial value. Initial intensities of brightness are converted to power by the illumination conversion factor 1 W = 685 lumen and expressed as radiant power, Q (microwatts). Relative intensities are expressed as a ratio to a magnesium salt of lysine succinate glass standard, Q/Q_{Mg}. No significant difference in intensity is observed under vacuum versus air and consequently all measurements are made under atmospheric conditions. X-ray diffraction data were collected on a Rigaku D/max-RBX rotating anode diffractometer using Cu Kα radiation (λ = 1.541 84 A, graphite monochromator). TGA and DSC data were collected on Perkin-Elmer Series 7 thermal analyzers.

Results

Various salts of lysine succinate were prepared by the addition of metal ions from the corresponding metal oxide. These salts are stable to microwave drying temperatures and no difference is observed between microwave or convection drying to remove water. All salts exhibit a negative dielectric increment with temperature which limits the maximal temperature achieved by microwave to <523 K which is below the thermal decomposition temperature (563 K). Table 1 indicates the relative intensities of room-temperature phosphorescence measured with a benchtop light meter for materials prepared with ions selected from several periodic groups. Two ions, Mg^{2+} and Zn^{2+} give the highest phosphorescence intensity. Emission intensity appears to decrease for metals within a given group as the molecular weight increases (Be in group II is an exception). It is observed that the intensity within each periodic group is related to the ionic size of the metal for group I and group II elements and the atomic charge. A maximum phosphorescence intensity occurs with ions having ionic radii between 0.66 and 0.77 Å.

The amount of amino acid required to form a glass matrix is shown in Figure 1. At a constant weight of the magnesium salt of succinic acid the amount of lysine monohydrate was increased from 0.1 to 45 wt %. The phosphorescence intensity of these materials indicates a transition from low-intensity to high-intensity emission occurs at about 35% lysine which corresponds to a 2/1 molar ratio of dicarboxylate salt to amino acid. Above this ratio the phosphorescence increases slightly.

Figure 2 shows the excitation spectrum and the total luminescence spectrum for the magnesium salt of lysine

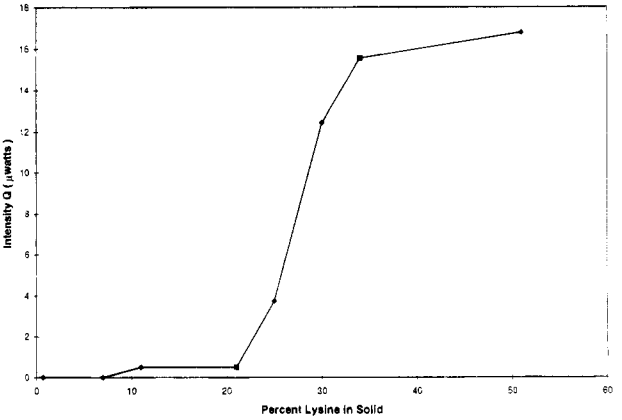

Figure 1. Radiant power, Q, of the magnesium-based phosphor for various amounts of lysine. The average of three intensity measurements from the illuminometer (see methods) are shown for each composition. The molar ratio of succinic acid and MgO were held constant at 1/1 as the amount of lysine monohydrate is added. Lysine content is expressed as grams of lysine (dry basis) per gram of solid (dry basis).

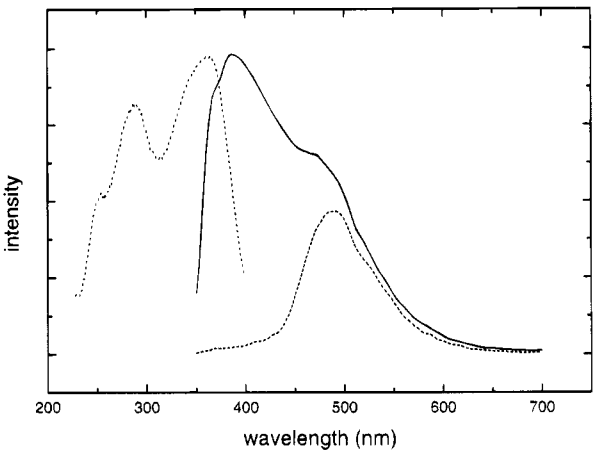

Figure 2. Room-temperature fluorescence excitation (dotted curve), total emission (solid curve), and phosphorescence spectra (dashed curve) of the solid magnesium salt of lysine succinate. Excitation of total emission and phosphorescence at 290 nm.

succinate. The total emission spectrum is composed of a short-lived fluorescence (lifetime of 10–20 ns) and a long-lived phosphorescence (1–2 s). The excitation spectra has maxima at 290 and 360 nm. The emission spectra (λ_{ex} = 290) shows a maximum fluorescence band at 400 nm and a phosphorescence band at 489 nm. Excitation at λ_{ex} = 365 moves the fluorescence to lower energy (λ_{emf} = 430 nm) but leaves the position of the phosphorescence band unchanged. An order of magnitude increase in the relative phosphorescence intensity of the 290 nm excited over the 365 nm excited glass is found. The emission properties of the zinc salt are similar but phosphorescence is shifted to the red by 15 nm. The spectrum of the phosphorescence intensity is similar to the spectral sensitivity of the scotopic eye. Corresponding measurements of brightness of the phosphors could be made with the light meter described in the Experimental Section. The excitation wavelength of 365 nm was chosen for these measurements.

The fluorescence and phosphorescence intensities from succinic acid and the metal oxides are negligible. Various lysine sources gave a fluorescence which varied between 2 and 6% of the magnitude of a lysine succinate

Table 2. Phosphorescence of Lysine-Based Materials with Various Metals and Carboxylic Acids[a]

		Mg		Zn		Ca	
carbon no.	acid	Q (μW)	τ (s)	Q (μW)	τ (s)	Q (μW)	τ (s)
C1	carboxylic	2.36(0.15)	1.41(0.05)	na[b]	na	na	na
C2	oxalic	0.67(0.37)	0.55(0.13)	na	na	na	na
C3	malonic	17.4(0.3)	1.67(0.09)	23.6(0.15)	1.27(0.05)	13.6(0.1)	1.59(0.04)
C4	succinic	15.1(0.1)	1.73(0.05)	25.0(0.15)	1.24(0.05)	1.28(0.27)	1.10(0.10)
C5	glutaric	25.9(0.1)	1.73(0.05)	30.7(0.15)	1.07(0.05)	2.37(0.37)	1.44(0.13)
C6	adipic	19.7(0.2)	1.64(0.08)	20.7(0.37)	1.01(0.13)	na	na
C7	pimelic	6.93(0.75)	1.33(0.26)	1.36(0.15)	1.24(0.05)	na	na
C8	suberic	3.21(0.10)	1.38(0.05)	2.03(0.27)	1.41(0.09)	na	na
C4	malic	6.59(0.27)	1.84(0.10)	6.10(0.24)	1.38(0.09)	1.35(0.50)	1.90(0.18)
C4	aspartic	8.80(0.75)	1.76(0.28)	4.23(0.16)	1.41(0.05)	2.20(0.42)	1.73(0.15)
C6	citric	4.06(0.50)	1.88(0.18)	4.39(0.25)	1.47(0.09)	na	

[a] Phosphors are prepared by dissolving 0.061 mol of lysine hydrate in 6 mL of water and adding 0.061 mol of the corresponding metal oxide and carboxylic acid (acid form except carboxylic in which metal carbonate was used. The material was dried 60 s in a standard microwave oven. For measurement 0.5 g of phosphor was placed in sample well of instrument described in the Experimental Section. The average of three replicates with standard deviation is shown in parentheses is given for intensity and lifetime. Values of fc are converted to radiant power, Q (microwatts, μW) by multiplying foot-candle values by the area of illumination (0.008 522 ft^2) and by the illumination convertion factor for brightness 685 lumen/W or 1 fc $\equiv$ 12.44 μW. [b] na indicates luminescence intensity below 0.01 fc on light meter.

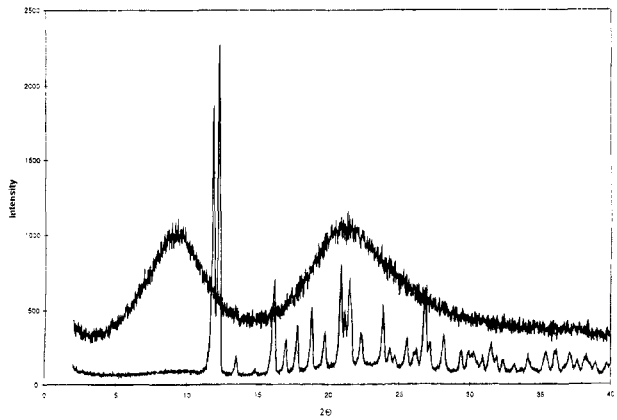

Figure 3. X-ray powder diffraction pattern (CuKα source) of two samples (squares) in Figure 2. Lower curve for sample with 21 wt % lysine, upper curve with 33 wt % lysine mixed and dried with magnesium succinate as described in methods. The amorphous pattern is typically observed for most materials listed in Table 2.

glass. Very weak phosphorescence is observed from various sources of lysine. This baseline phosphorescence, which could not be removed by recrystallization or solvent extraction, is <1.5% of the magnitude of a lysine succinate glass.

Figure 3 shows X-ray diffraction patterns of the materials before and after the transition to a high-intensity phosphor. Materials found to be efficient phosphors are noncrystalline as indicated by the broad structureless X-ray pattern. All phosphors of high relative intensity in Table 1 ($Q/Q_{Mg} > 0.5$) salts are amorphous. An anomalous pattern has been observed for the Be salt which shows only one amorphous band at the higher angles and for which $Q/Q_{Mg} < 0.5$. Mixed crystal and noncrystalline patterns are found for Ca, and Sr salts $0.1 < Q/Q_{Mg} < 0.5$. Intense crystalline bands are observed for Na and K salts, $Q/Q_{Mg} < 0.1$ which correspond to a mixture of bands observed for the pure crystalline forms of lysine monohydrate and succinic acid.

The lysine succinate salts are among a class of materials which show photoluminescent properties. Several other lysine salts of various carboxylic acids have been prepared. Table 2 indicates a series of materials containing Zn, Mg, and Ca ions. The intensity of the phosphorescence is maximal in the range of C3–C6 acids with a slight maximum for C5 dicarboxylic acids for Zn and Mg and a maximum for the C3 acid when Ca is used. All materials with measurable photoluminescent properties in Table 2 ($Q > 2$) are amorphous on X-ray diffraction. Materials with moderate values, $0.5 < Q < 2.0$, show a mixture of sharp, intense X-ray lines associated with either the organic acid or amino acid and diffuse, weak bands associated with the glass state.

Three monocarboxylic acids, formic acid and acetic acid, and carbonate produce photoluminescent materials with lysine. Carbonate forms active materials only with magnesium and not with zinc or calcium. Twice the molar ratio of formate/lysine and acetate/lysine is required with the magnesium and zinc salts than for the corresponding dicarboxylic acids to achieve a maximal photoluminescence. Derivatives of succinic acid such as hydroxysuccinic (malic), aminosuccinic (aspartic acid), and tricarboxylic acids (citric) also produce photoluminescent materials (Table 2). Various ketoacids (α-ketobutyric, α-ketoglutaric, oxaloacetic) and unsaturated dicarboxylic acids (itaconic, fumaric, and maleic acids) did not make a photoluminescent product. X-ray studies indicated that the material prepared from the magnesium salt of lysine fumarate was amorphous, which suggests some alternative mode of deactivation from the excited state.

Other amino acids in their naturally purified state were also explored. The related amino acid ornithine gave compounds with luminescent intensities about an order of magnitude less than the corresponding lysine compound. The precursor to lysine in the bacteria synthetic pathway, diaminopimelic acid (DAP), gave strong phosphorescence intensities similar to lysine. Other amino acids such as arginine, tyrosine, aspartic acid, glutamic acid, and tryptophan did not substitute for lysine. Glasses could be formed from magnesium succinate and several amino acids including glycine, β-alanine, and γ-aminobutyric acid. These amino acids are unbranched and have a linear carbon chain separating the carboxyl and amino ends. Unlike lysine and DAP, these glasses did not show intrinsic luminescent properties. The dibasic amino acids, aspartic and glutamic acid, were the only amino acids found which could substitute for succinic acid in the presence of

lysine to produce photoluminescent materials. This observation suggests a unique electronic environment may be found for proteins in which lysine interacts with aspartic and glutamic acid via electrostatic interactions or by metal complexation.

The lifetimes of the room-temperature phosphorescence reported in Table 2 range from 1 to 2 s. In all cases the visual lifetime is longer and extends for about 20−25 s. In general, lifetimes of the zinc salts were found to be shorter than the magnesium and calcium salts. The intensity and lifetimes are not changed by repeated dissolution of these phosphors in hot water and drying. Room-temperature phosphorescence was observed from glasses containing up to 12 wt % water (3 mol of water/mol of lysine). Although room-temperature phosphorescence is quenched for most of these materials at >15% water, several glasses could be prepared which were phosphorescent while hydrated with 70% water.

Discussion

Molecular substances can be embedded in a glass structure and immobilized, restricting rotational, and translational diffusional processes. These processes are responsible for radiationless decay of energy from entrapped molecules in the excited singlet or triplet states. The molecular environment of lysine with various oxyanions in the solid state has been studied.[29] The molecules aggregate to form an S2 head-to-tail sequence connected by interactions between the side chain amino group and a neighboring α-carboxylate oxygen.[30] The interacting organic component forms a suitable environment for a network-modifying ion such as magnesium to create the amorphous state. Magnesium can exclusively form octahedral hexacoordinated complexes with ligands. The crystal structure of lysine succinate shows a cavity approximately 7 Å in width between the carbon skeletons of lysine and succinate in which the metal can coordinate. Larger ions such as calcium or sodium can distort the ligand interactions and tend to crystallize as the metal complex of the organic acid.

If the luminescence occurs from this coordination sphere, then it is also responsible for increased absorption into an excited singlet state and subsequent fluorescence. The size of the coordination center influences the efficiency of both fluorescence and phosphorescence. From the data in Table 2, the energy transferred and emitted from a triplet state can be calculated from the product $Q^*\tau$ (μJ). For example, comparing C6 (adipic) and C7 (pimelic) acids a 3.5-fold decrease in energy occurs for the Mg salt and a 12.4-fold decrease for the Zn salt, indicating a high sensitivity of the C7 triplet state environment to zinc. A decrease of several orders of magnitude occurs between the Mg salts and the Ca salts suggesting either a reduced rate of intersystem crossing or an alternate mechanism for deactivation of the excited state.

An intrinsic coordination center for luminescence may reside with the organic acid. The lifetime and color of the luminescent glasses compare to that of phosphorescent studies in liquid oxygen reported 40 years earlier for the series of dicarboxylic acids, oxalic, malonic, succinic, glutaric, and adipic acid.[31] Only the electronic states and luminescent properties of oxalic acid and derivatives in the glassy state at 77 K have been studied in detail.[32]

The presence of reaction products or trace impurities contributing to luminescence cannot be discounted. The chemical combination of a diamine and dicarboxylic acid to form nylon salt precursors and subsequent polymerization to nylon is possible with lysine.[33] Intrinsic luminescence has been previously reported from the structure of nylon polymers.[34,35] Polymerization products however have not been detected from biochemical, HPLC, and NMR analysis of the products which show >99% recovery of the free amine groups and succinate ion. This does not preclude a 5−500 ppm concentration of a molecular species capable of fluorescence and phosphorescence. A fluorescing species which is sensitive to thermal history of the amino acid is found in fermentation-derived preparations of lysine but has been unidentified. HPLC indicates ppm amounts of aromatic amino acids phenylalanine and tryptophan in this preparation which do not contribute to the phosphorescence. Yellow pigments are known to occur during fermentation of lysine from *Corynbacteria*.[36] Although the thermal degradation pathway of lysine is known to produce aromatic compounds such as pyridines,[37] these materials have been tested and do not show luminescence. It has been reported that the commercial origin of lysine and other amino acids plays a role in the intensity of lyoluminescence.[38] The presence of similar luminescent behavior for synthetic and fermentation-derived lysine obtained from various plant sources and microorganisms does not support a conclusion of a single impurity derived from the production of the amino acid.

Physical properties of the glass state and changes associated with the solid state have been studied by thermal analysis. The thermal properties of metal salts of succinic acid have been previously reported.[39] The magnesium and cobalt salts when heated above 430 K become amorphous as evidenced by X-ray diffraction. An exothermic transition due to recrystallization from the glass state is seen by DSC at 583 K. Magnesium salts of succinic acid which contain lysine indicate that this transition is present up to 25% lysine (Figure 1). At a 2/1 molar ratio of succinic acid/lysine the DSC scan is altered as evidence by the disappearance of the exothermic transition at 583 K and the appearance of endotherms at 393 K which correspond to a glass transition. The inability of the glass to recrystallize is a demonstration of the stability of this glass state.

The phosphorescence of lysine salts or dicarboxylic acids is extremely sensitive to slight changes in the

(29) Prasad, G. S.; Vijayan, M. *Acta Crystallogr.* **1991**, *B47*, 927.
(30) Suresh, C. G.; Vijayan, M. *Int. J. Pept. Protein Res.* **1983**, *22*, 617.
(31) Vishnevskii, A. P. *Dokl. Akad. Nauk. SSSR* **1948**, *63*, 503.
(32) Maria, H. J.; McGlynn, S. P. *J. Mol. Spectrosc.* **1972**, *42*, 296.
(33) Nagata, M.; Kiyotsukuri, T.; Kohmoto, D.; Tsutsumi, N. *Eur. Polym. J.* **1994**, *30*, 135.
(34) Allen, N. S.; Harrison, M. J. *Eur. Polym. J.* **1985**, *21*, 517.
(35) Allen, N. S.; Ledward, M.; Follow, G. W. *Eur. Polym. J.* **1990**, *26*, 237.
(36) Kawakita, T.; Koga, Y.; Saeki, M. *Agric. Biol. Chem.* **1989**, *53*, 3301.
(37) Breitbart, D. J.; Nawar, W. W. *J. Agric. Food Chem.* **1979**, *27*, 511.
(38) Galand, E.; Niezette, J.; Vanderschueren, J.; Garsou, J.; Hoebeke, M. *Radiat. Phys. Chem.* **1994**, *43*, 377.
(39) Nagase, K.; Yokobayashi, H.; Muraishi, K.; Sone, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1612.

structure of the acid or the alkaline earth metal used. For example, π-bonded linear acids shut off luminescence as indicated by the magnesium salt of lysine succinate (saturated four-carbon carboxylic acid) which shows luminescent properties whereas, the salt of lysine fumarate (unsaturated four-carbon acid) does not. Other examples include substitution of ketoacids for saturated carboxylic acids (ketobutyric/succinic, oxaloacetic/oxalic) and differences among a series of linear saturated acids (Table 2). The ability to control luminescence in the solid state by chemical modifications in the network-forming chemicals offers the materials scientist a new tool for the preparation of interesting optical materials of biological origin and the spectroscopist the opportunity to explore the interaction of molecular solids with light.

Acknowledgment. The authors acknowledge funding of this project from the United States Department of Agriculture and the Kellogg Foundation. We thank Mr. Paul Nowaczyk for initial studies on lysine succinate salts. We acknowledge the determination of fluorescence lifetime and spectral studies by Dr. Tom Carter of the Laser Laboratory at Michigan State University and the assistance of Dr. Alex Scranton in the Department of Chemical Engineering at MSU.

CM940440N