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ZEOLITE-SUPPORTED TETRAMETHYL-1,2-DIOXETANE: NEW PATHWAYS TO CHEMILUMINESCENCE

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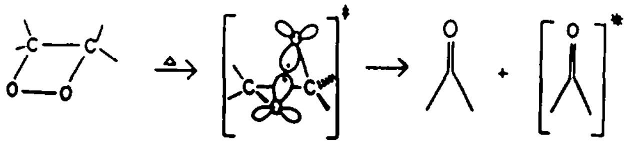
Abstract - The thermal decomposition of tetramethyl-1,2-dioxetane (TMD) sorbed into zeolite Y containing Eu^{3+} ions and 2,2'-bipyridine (samples abbreviated as ZYEBT) has been investigated. Decomposition of TMD yields, by energy transfer processes, chemiluminescence (CL) characteristic of the Eu^{3+} ion. At loading levels corresponding to an upper-limit average of 0.5, 1.0, and 2.0 TMD molecules per unit cell, the CL decay curves are nonexponential at short times; at longer times, roughly exponential curves are characterized by a unimolecular rate constant k. Analyses of the long-time decays based on an Arrhenius expression for the rate constant provide evidence for a kinetic compensation effect: plots of log k vs. the activation energy E_a as a function of TMD loading level are linear. Solution data (benzene, benzonitrile) fall on the same line, suggesting that TMD decomposes by a common rate-limiting mechanism in these various environments. The Arrhenius parameters (E_a and the pre-exponential factor A) are smaller than the solution values and increase with TMD loading. When TMD is sorbed to the extent of an upper-limit average of $\sim$7 molecules per unit cell, CL decay curves are initially nearly flat and then show an increase in decomposition rate with time. Mechanistic implications of these results are discussed.

In recent studies we have examined the effects of adsorption onto silica gel and intercalation into a layered solid, hydrogen uranyl phosphate (HUP), on the excited-state processes of organic and inorganic compounds. In the former case, the photoisomerization of retinal isomers,[1] the loss of CO from (η^6-arene)tricarbonylchromium(0) complexes,[2] and the luminescence and photodimerization of a dibenzylideneacetone derivative[3] are all perturbed by adsorption. Intercalation of guest species such as $Cr(NH_3)_6^{3+}$ and Eu^{3+} into HUP has provided evidence of efficient host-to-guest, excited-state energy transfer processes.[4,5]

In considering compounds whose excited-state properties might be sensitive to their environment, our attention was drawn to tetramethyl-1,2-dioxetane (TMD). As shown in eq. (1), TMD thermally


(1)

decomposes to yield an excited acetone molecule; chemiluminescence (CL) has been observed from this species (acetone fluorescence and phosphorescence)[6] and from suitable acceptor species such as Eu^{3+} complexes.[7,8] The reaction is sterically demanding. A calculated transition state is characterized by a twisting of the peroxy ring.[9] The steric demands of the decomposition have prompted us to introduce TMD into zeolites where the host cage structure can impose its own steric constraints on the decomposition.

In this paper, we report that TMD can be sorbed in varying quantities into zeolite Y containing Eu^{3+} ions and 2,2'-bipyridine. Thermal decomposition of TMD in this host (abbreviated ZYEBT) produces, by energy-transfer processes, CL characteristic of the Eu^{3+} ions. Kinetic analysis of CL decay curves indicates that TMD occupies sites of varying reactivity in the solid. An Arrhenius treatment of the exponential portion of CL decay curves, characterized by a unimolecular rate constant k, is consistent with a kinetic compensation effect: plots of log k vs. the activation energy E_a are linear for various TMD loading levels. Moreover, solution data are fit by the same line, suggesting a common rate-limiting mechanism in these diverse environments. Evidence for a cooperative decomposition mechanism is seen at the highest TMD loading level examined.

RESULTS AND DISCUSSION

In sections below we describe the preparation and characterization of zeolite-supported TMD, its chemiluminescent properties, and the mechanistic implications of these properties.

Preparation and Characterization of Zeolite-Supported TMD. The host solid for our studies, zeolite Y, was calcined at 500°C prior to use. As sketched in Figure 1, an average unit cell of this zeolite, $Na_{57}[(AlO_2)_{57}(SiO_2)_{135}]\cdot xH_2O$, has a pore diameter of 7.4 Å and a cavity diameter of 13 Å. Initial experiments, wherein TMD was sorbed into the zeolite from benzene solution, yielded CL signals that were too weak for kinetic analysis.

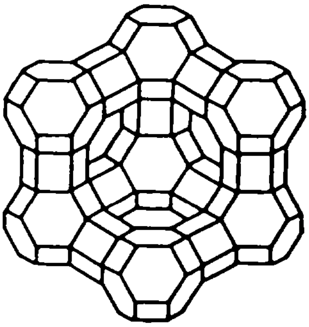


Fig. 1. Sketch of a portion of the unit cell of zeolite Y (faujasite structure). Vertices are Si or Al atoms that are tetrahedrally coordinated by O atoms.

Since Eu^{3+} complexes are known acceptors for dioxetane CL,[7,8] the lanthanide ion was exchanged into the zeolite from aqueous solution to the extent of about one ion per unit cell. After drying (200°C at 4 x 10^{-5} torr for 24 h), the zeolite exhibited weak pink photoluminescence (PL) characteristic of Eu^{3+} when irradiated with near-UV light. Sorption of TMD from CH_2Cl_2 solution into the exchanged zeolite yielded pink CL on warming, but of insufficient intensity for kinetic analysis. The weak PL and CL signals may be due to the presence of water molecules in the metal ion's coordination sphere, since O-H stretching modes are known to serve as efficient nonradiative decay routes.[10,11] Alternatively, the weak CL intensity may result from the presence of transition metal impurities. These species could catalyze the decomposition of TMD in the zeolite, as they do in solution.[12]

In an effort to improve the radiative efficiency of the Eu-exchanged zeolite, the solid was exposed to an ethanolic solution of 2,2'-bipyridine with the expectation that the sorbed species would chelate to Eu^{3+}, displacing water molecules. Indeed, sorption causes the radiative efficiency to increase substantially and results in a sample PL lifetime of ~1.2 msec. From correlations previously reported for Eu-exchanged zeolites, this lifetime corresponds to essentially complete loss of water from the Eu coordination sphere.[13] Heating this sample under vacuum (10^{-4} torr at 150°C for 12 h) does not affect the PL lifetime but does remove excess bipyridine that could block channels into the zeolite system, obstructing TMD sorption. Spectrophotometric analysis of these samples after dissolution in HF indicated the presence of ∿2.6-2.8 bipyridine molecules per unit cell and hence per Eu^{3+} ion. From this stoichiometry we suspect that, on average, the Eu^{3+} ions are coordinated to two bipyridine ligands with the balance of the coordination sites occupied by lattice oxygen atoms. Consistent with such a bonding scheme is the observation that a nitrate salt of Eu containing two bipyridine ligands in the coordination sphere, $Eu(bpy)_2(NO_3)_3$,[14] yields an identical lifetime within experimental error. A noteworthy feature of chelation is that it helps prevent migration of Eu^{3+} ions out of the zeolite cages on steric grounds. Moreover, chelation can serve to diminish the role of impurity metals present in the zeolite that could otherwise catalyze the decomposition of TMD.[12]

Once dried, the Eu-exchanged zeolite containing bipyridine was slurried with chilled CH_2Cl_2 solutions of TMD. The concentrations of TMD were such that complete uptake would correspond to sorption of 0.5, 1.0, and 2.0 TMD molecules per unit cell on average. Although TMD uptake appeared to be essentially complete (based on negligible quantities of acetone in the filtrate, assayed by infrared spectroscopy following refluxing of the filtrate with $CuBr_2$ as a decomposition catalyst), these concentrations should be regarded as upper limits, since some decomposition may accompany sorption. Incomplete sorption from a more concentrated TMD solution resulted in samples with an upper-limit average of ∿7 TMD molecules per unit cell. It is worth emphasizing that we do not know where the TMD molecules reside within the zeolite cages, nor can we exclude the possibility that some of the molecules are present on the external surfaces of the zeolite.

Chemiluminescent Properties. Samples of zeolite Y containing Eu^{3+}, bipyridine, and TMD (denoted as ZYEBT) exhibit intense pink CL when heated above ∿65°C. The emission is readily seen by the dark-adapted eye. At lower temperatures the CL intensity declines sufficiently slowly that a steady-state CL spectrum can be obtained. Figure 2 reveals that the spectral distribution consists of the sharp f-f transitions characteristic of Eu^{3+}. Moreover, the spectrum is blank at wavelengths below 550 nm where acetone fluorescence and phosphorescence would normally be observed, consistent with energy transfer to Eu^{3+} in ZYEBT.

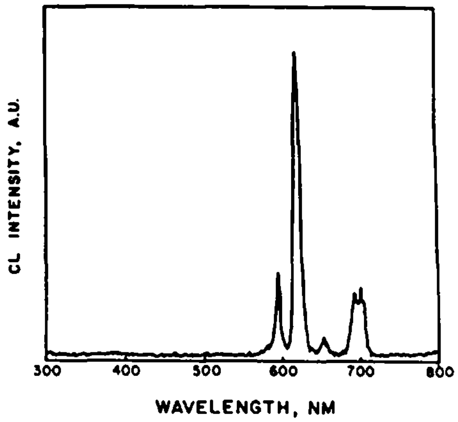


Fig. 2. Chemiluminescence spectrum of a sample of ZYEBT (upper-limit average loading of 1.8 TMD molecules per unit cell; average of ∿2.6 bipyridine molecules per unit cell) obtained at 53°C. The spectrum is a composite of two scans from 300-500 and 500-800 nm.

The intensity of the CL is presumed proportional to TMD concentration, as is found in solution studies,[15] and provides a probe of the kinetics of TMD decomposition in ZYEBT. Plots of CL intensity as a function of time generally show a slight increase at short times, presumably reflecting the approach to the thermostatically-controlled decomposition temperature, followed by a monotonic decline. Figure 3 shows a plot of ln (CL intensity) vs. time for one ZYEBT sample at 64°C. As shown in the figure, there is often some curvature present in the early-time portion of the plots, indicating that the rate of TMD decomposition is greatest in this temporal regime; the curvature becomes less apparent with increasing temperature. As will be discussed in more detail below, the curvature is consistent with the presence of different environments (within the cages and/or on the external surfaces) for TMD in ZYEBT.

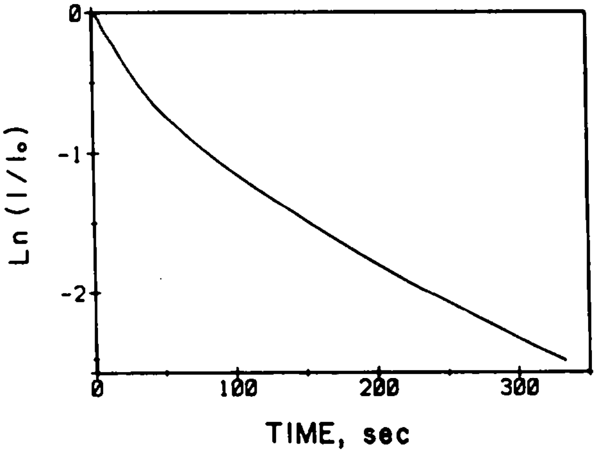


Fig. 3. Plot of ln (CL intensity) as a function of time for a ZYEBT sample having an upper-limit average loading of 0.5 TMD molecules per unit cell and ~2.6 bipyridine molecules per unit cell. Data were obtained at 64°C.

At longer times, the CL decay curves are roughly exponential, as shown in Figures 3 and 4 for several ZYEBT samples: decay can be described by a single, unimolecular rate constant k that varies with the TMD loading level. Data from the linear regime can be fit by an equation based on the Arrhenius expression, eq. (2),

$$\log k = \log A - E_a/2.3RT \qquad (2)$$

where k is the first-order rate constant, A is the pre-exponential factor, E_a is the activation energy for the process, and R is the gas constant.

As shown in Figure 5 for a representative sample, plots of log k vs. T^{-1} are linear for the temperature range over which CL decay data can be acquired. The values of E_a and log A, extracted from the slopes and intercepts of the Arrhenius plots, respectively, are presented in Table 1 along with solution data, which, for benzene, are in reasonable accord with literature values.[16] Note that both E_a and log A increase with TMD loading level and in all cases are lower than their solution counterparts.

For the highest loading level, corresponding to an upper-limit average of ~7 TMD molecules per unit cell, non-Arrhenius behavior is found, as shown in Figure 6. For this system, the plot of ln (CL intensity) vs. time is initially relatively flat and then exhibits an increase in decomposition rate with time.

We also attempted to assess whether the Eu complex presumed present in the zeolite could catalytically decompose TMD. To test this possibility, the rates of TMD decomposition were determined in benzonitrile solution using $Eu(bpy)_2(NO_3)_3$ (0.17 and 0.34 mM) and 9,10-dibromoanthracene (DBA; 0.17 mM) as energy acceptors; in the DBA experiment, EDTA was also present to sequester trace metal impurities that could catalyze the decomposition. We found that the rates were identical for the two acceptors within experimental error.

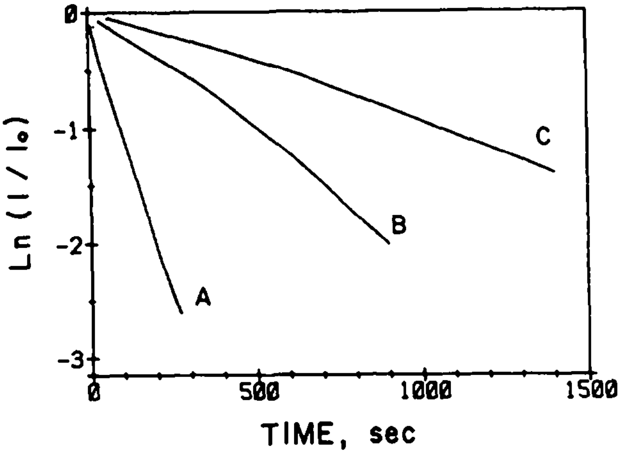


Fig. 4. Plots of ln (CL intensity) as a function of time for ZYEBT samples having upper-limit average loadings of 0.5 (curve A), 1.0 (curve B), and 2.0 (curve C) TMD molecules per unit cell; an average of ~2.8 bipyridine molecules per unit cell were present in the sample. Data were obtained at 60°C and are normalized to a common initial intensity.

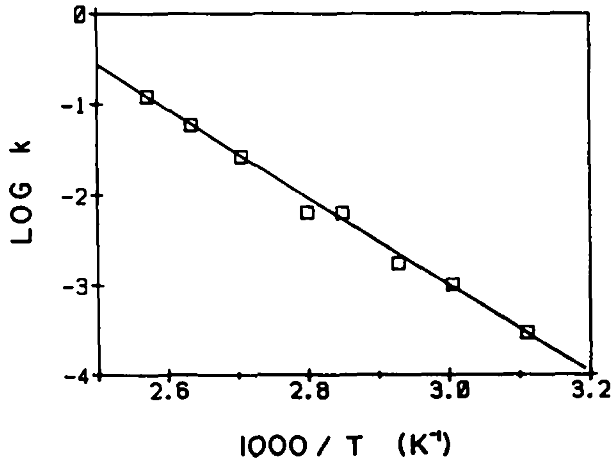


Fig. 5. Plot of log k vs. reciprocal temperature for a ZYEBT sample having an upper-limit average loading of 2.0 TMD molecules per unit cell and an average of ~2.8 bipyridine molecules per unit cell. Values of k were extracted from the exponential portion of CL decay curves like those shown in fig. 4.

We sought additional evidence for the absence of a catalyzed decomposition from relative CL efficiencies; we would expect comparable solution and ZYEBT values if the mechanism were the same. When the integrated CL decay from a benzonitrile solution containing 18 mM TMD and $Eu(bpy)_2(NO_3)_3$ (nearly saturated; ~0.2 mM) was compared to that from a ZYEBT sample with 1.0 TMD molecule per unit cell on average (representing a similar TMD concentration), the former produced more light by a factor of about 40. While these values seem quite disparate, the fact that the sorbed TMD concentration is an upper limit and that light is less efficiently collected in the zeolite experiment due to scattering could conceivably lead to similar CL efficiencies. Collectively, then, our data suggest that $Eu(bpy)_2(NO_3)_3$ does not catalyze TMD decomposition. However, other

Eu complexes may be present and the possibility of catalytic decomposition in the zeolite cannot be excluded.

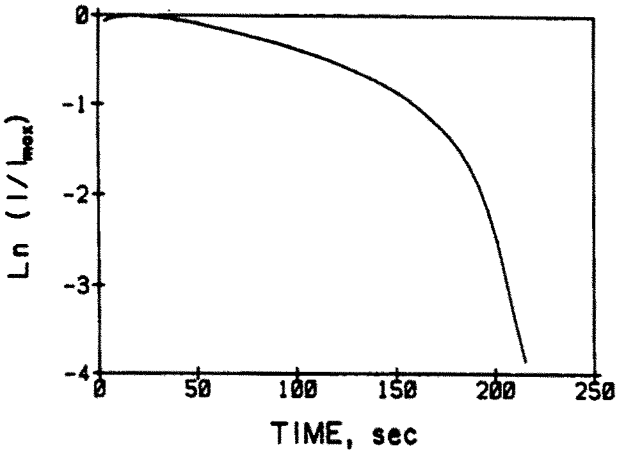


Fig. 6. Plot of ln (CL intensity) as a function of time for a ZYEBT sample having an upper-limit average loading of ∿7 TMD molecules per unit cell and an average of ∿2.6 bipyridine molecules per unit cell. Data were obtained at 80°C.

Mechanistic Implications. The significance of the data collected in Table 1 is highlighted in Figure 7. Plots of log k vs. E_a for TMD decomposition in the various environments described in the table show a reasonable fit to a straight line; data for three temperatures are plotted and roughly intersect at log A = 2.3 (the last term of eq. 2 is zero). This linearity, also observed in a plot of E_a vs. log A, has conventionally been a diagnostic test for the existence of a kinetic compensation effect: when experimental conditions result in a change in the enthalpy of activation there is a corresponding linear change in the entropy of activation.[17-20] Decomposition of TMD in various solvents has previously been shown to lead to a linear relationship between the enthalpy and entropy of activation.[21] Underlying a kinetic compensation effect would be a common rate-limiting mechanism that is independent of the reaction environment.

Table 1. Arrhenius parameters for the decomposition of TMD in ZYEBT samples[a]

Environment[b]	E_a, kcal/mol[c]	log A, sec^{-1}[d]
ZYEBT-0.5	18.6	10.2
ZYEBT-1.0	19.9	10.6
ZYEBT-2.0	22.2	11.5
benzene	25.7	13.0
benzonitrile	27.2	13.7

[a] Arrhenius parameters for the decomposition of TMD determined from plots of log k vs. T^{-1} as given by eq. 2 and illustrated in fig. 5; values of k in sec^{-1} are obtained from the decay of chemiluminescence, as illustrated in fig. 4.

[b] Environment in which TMD decomposition takes place. The first three entries are samples of zeolite Y containing Eu^{3+} ions, bipyridine (an average of ∿2.8 molecules per unit cell), and TMD (ZYEBT); the number following this designation denotes the upper-limit average number of TMD molecules per unit cell. The last two entries represent homogeneous solution data obtained in the indicated solvent.

[c] Activation energy, obtained from the slope of log k vs. T^{-1} plots (eq. 2). Values have errors of ±0.7 kcal/mole.

[d] Pre-exponential factor, obtained from the intercept of log k vs. T^{-1} plots (eq. 2). Values have errors of ±0.3.

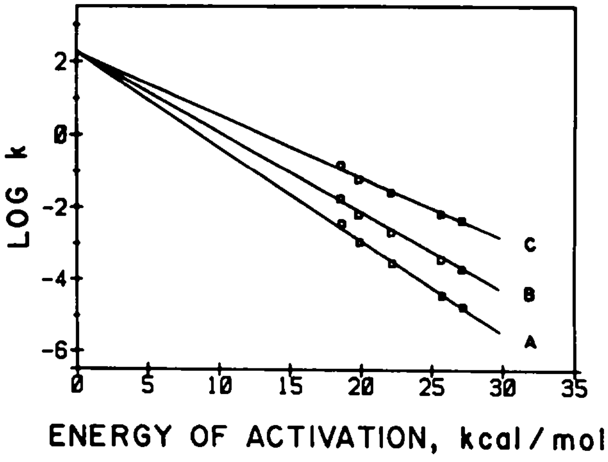


Fig. 7. Plot of log k vs. activation energy for TMD decomposition in various environments at 49 (curve A), 69 (curve B), and 96°C (curve C). For each curve, the points from left to right correspond to ZYEBT samples with upper-limit average loadings of 0.5, 1.0, and 2.0 TMD molecules per unit cell and solution data in benzene and benzonitrile solution, respectively; the ZYEBT samples have an average of ∿2.8 bipyridine molecules per unit cell.

For the system at hand, we presume the common rate-limiting mechanistic step to be the bond-breaking leading to ring cleavage. The reduction in E_a in passing from solution to the zeolitic environment may be a reflection of the strong electrostatic forces present in the cage; the compensating reduction in log A indicates that this lowering of the barrier to decomposition occurs at the expense of an increase in ordering, i.e., a more demanding geometry is involved. It is noteworthy that all of the ZYEBT samples exhibit negative entropies of activation, indicating that the systems become more ordered upon passage to the transition state.

The increase in E_a and log A with TMD loading into ZYEBT also merits comment. One possible explanation is that as the space available in a cage to an individual TMD molecule decreases, the energy of activation required to place the molecule in the transition state configuration increases; beginning with a more ordered environment will also cause the entropy term to increase.

Particularly intriguing is the non-Arrhenius behavior seen at the highest loading level employed, Figure 6. We suspect that the initial flatness of the ln (CL intensity) curve and subsequent increase in decomposition rate with time reflects a cooperative interaction among the relatively dense-packed TMD molecules. One scenario leading to a curve like that shown could involve the sequential decomposition of TMD molecules within a cage: if steric constraints have to be relieved for decomposition to proceed, then as each molecule decomposes, the remaining TMD molecules can more easily decompose by virtue of replacing TMD molecules with smaller, more mobile acetone molecules.

We believe that crowding of TMD molecules may also be reflected in the short-term, nonexponential decay seen in CL decay curves at lower loading levels, illustrated in Figure 3. Qualitatively, the nonlinearity indicates that some fraction of TMD molecules reside in sites leading to relatively rapid decomposition. That these might be sites of crowding is consistent with a quantum chain decomposition mechanism proposed to account for non-Arrhenius CL decay at high concentrations in solution.[15] The key mechanistic step is presumed to be the attack of an excited acetone molecule on TMD, eq. (3).

$$\text{acetone}^* + \text{TMD} \longrightarrow \alpha\ \text{acetone}^* + (3-\alpha)\text{acetone} \qquad (3)$$

Alternatively, the sites of rapid decomposition may be positions proximate to an adventitious catalyst present in the zeolite.

Determination of the volume of activation accompanying TMD decomposition should provide a better idea of the molecule's steric demands. Using average number of molecules sorbed as a measure of pressure, the increase in decomposition rate at a given temperature with a decrease in loading (fig. 7) corresponds to a positive volume of activation for decomposition in ZYEBT, as was found in solution studies.[22] However, the uncertainty in sorbed concentration precludes a quantitative estimate.

In summary, TMD can be incorporated into zeolite Y containing Eu^{3+} ions and bipyridine (ZYEBT samples). Thermal decomposition of TMD yields chemiluminescence characteristic of the lanthanide ion via energy transfer processes. Kinetic decay parameters obtained from CL measurements at various TMD loading levels in ZYEBT and in solution provide evidence for a kinetic compensation effect, indicative of a common rate-limiting, bond-cleavage mechanism. The demonstration that a zeolite can substantially influence the decomposition kinetics of TMD is worthy of more general examination, since zeolite-dioxetane combinations of varying steric constraints are realizable. It may be possible to substantially retard dioxetane decomposition in desired temperature regimes through zeolitic incorporation.

EXPERIMENTAL

Sample preparation. Zeolite Y was obtained from the Linde Division of Union Carbide Corp. and calcined at 500°C prior to use. Exchange of Eu^{3+} into the zeolite was accomplished by slurrying 6.9 g ($\sim 5.3 \times 10^{-4}$ mol) of the solid in 64 mL of triply-distilled water that was subsequently brought from pH 10.5 to 5.5 by the dropwise addition of conc. HNO_3. To this slurry was added 5 mL of a 97 mM $Eu(NO_3)_3$ (Alfa) solution. Complete exchange of available Eu^{3+} for Na^+ results in an average of approximately one Eu^{3+} ion per unit cell of zeolite Y. After allowing exchange for 24 h, the slurry was filtered and dried in air at 100°C for 12 h; the residue from the evaporated filtrate showed negligible luminescence under near-UV excitation, consistent with essentially complete exchange. After drying, the sample was crushed and further dried at 200°C at 4×10^{-5} torr for 24 h. Once dried, the zeolite was placed in 50 mL of dry ethanol to which was added 2.4 mmol of 2,2'-bipyridine (Aldrich). Sorption was permitted to occur for 24 h after which the solid was removed and heated at 150°C at 10^{-4} torr for 12 h. This treatment removes uncomplexed 2,2'-bipyridine: the quantity present before and after heating was assayed by dissolving portions of the solid in conc. HF and spectrophotometrically analyzing for bipyridine (λ_{max} = 300 nm; ϵ = 14,900 $M^{-1}cm^{-1}$). After the aforementioned heat treatment, there were typically an average of $\sim$2.6-2.8 bipyridine molecules per unit cell. Samples were stored in a glove bag under dry N_2 until needed. Tetramethyl-1,2-dioxetane (TMD) was prepared as described in the literature.[23] The product's identity was established by its m.p. and ^1H NMR spectrum.[23] The compound was stored at -20°C until needed.

Sorption of TMD into the zeolite supports was accomplished by slurrying 0.2 g of the zeolite in 0°C CH_2Cl_2 solutions (4 mL) of TMD for 10 min.; concentrations of TMD were such that complete uptake would correspond to an average of about 0.5, 1.0, and 2.0 TMD molecules per unit cell. After 10 min., the slurry was filtered under N_2 and rinsed with 1 mL of cold CH_2Cl_2. The caked solid was broken up under dry N_2, allowed to stand for 1 min. to permit solvent evaporation, and put into chilled vials for storage at -78°C. The quantity of TMD remaining in solution was assayed by diluting the filtrate to 10 mL and refluxing for 12 h with $CuBr_2$ (Baker), a catalyst for TMD decomposition,[12] to convert any remaining TMD to acetone. The filtrate was analyzed by infrared spectroscopy (Beckman Model 4250) using 0.10-mm pathlength cells; a calibration curve was constructed from CH_2Cl_2 solutions containing known quantities of acetone. For all of the aforementioned sorption experiments, sorption appeared essentially complete based on the negligible quantity of acetone seen in the infrared spectrum. With a more concentrated TMD solution, corresponding to an average of 20 TMD molecules per unit cell, the sorption was incomplete; the maximum uptake of TMD corresponded to an average of $\sim$7 TMD molecules per unit cell. A sample of $Eu(bpy)_2(NO_3)_3$ was prepared as described in the literature.[14]

Chemiluminescence measurements. Samples of ZYEBT (zeolite Y containing Eu^{3+}, bipyridine, and TMD, prepared as described above) were placed in quartz capillary tubes (i.d. 1.5 mm) under dry N_2 and sealed with a septum. The sample tubes were kept at -78°C until ready for use. A steady-state chemiluminescence (CL) spectrum was obtained using a McPherson 0.35-m monochromator equipped with a IP-928 PMT and a LeCroy discriminator/counter. A ZYEBT sample (upper-limit average of $\sim$1.8 TMD molecules per unit cell; average of $\sim$2.6 bipyridine molecules per unit cell) was immersed in a thermostatic bath and heated to 53°C; the temperature of the bath was regulated by an Omega temperature controller to ± 0.2°C and calibrated against melting point standards. The CL signal was brought to the monochromator using a fiber optic cable. At 53°C, a full CL spectrum was obtained from composite spectra that were recorded from 300-500 nm and from 500-800 nm (two samples) with minimal loss in intensity. Chemiluminescence decay curves as a function of temperature were acquired using the same instrumentation employed for the steady-state spectra; CL intensity was monitored at 615 nm. The decay curve for each TMD loading level was examined at at least eight different temperatures, typically spanning a range of 48-115°C. Runs were made in triplicate. Data analysis was performed using an Apple IIe microcomputer, Numonics Corp. graphics calculator, and Houston Instruments DMP-40 plotter. Data were also obtained for TMD decomposition in homogeneous solution using benzene (Aldrich) and benzonitrile (Alfa) as solvents with 9,10-dibromoanthracene (DBA; Aldrich) as the energy acceptor and EDTA (Aldrich) to scavenge metal impurities.[12] The concentrations of TMD and DBA in these experiments were 10 and 2 mM, respectively; the solutions were saturated with EDTA. Evaluation of $Eu(bpy)_2(NO_3)_3$ as a catalyst for TMD decomposition was performed in two ways. First, the decomposition rates of 0.5 mM TMD benzonitrile solutions were determined with DBA (0.17 mM; solution also saturated with EDTA) and $Eu(bpy)_2(NO_3)_3$ (0.17 and 0.34 mM) as acceptors at 74.0 and 81.6°C, using instrumentation previously described for CL measurements; the CL was monitored at 615 and 439 nm for the Eu complex and DBA, respectively. In a second experiment, solution and zeolite CL efficiencies were compared. Using a common geometry employing a 1.0-mm pathlength cuvette, the CL decay curve of a ZYEBT sample with an average of 1.0 TMD molecule per unit cell was compared with that of a benzonitrile solution containing TMD (18 mM) and $Eu(bpy)_2(NO_3)_3$ (nearly saturated; ~0.2 mM) as the acceptor. Integration of the intensities was done by cutting and weighing the decay plots.

Lifetime measurements. Photoluminescence lifetime measurements of various Eu^{3+}-containing samples were made using instrumentation previously described.[5] Emission was excited at 337 nm and detected at 615 nm.

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