J. Phys. Chem. A **2005,** *109,* 2459−2464

Anomalous Green Emission and Energy Transfer in the *N*,*N*-Dimethylformamide/Hydrochloric Acid/Europium Chloride System

O. P. Dimitriev* and V. V. Kislyuk

Institute of Semiconductor Physics, National Academy of Sciences of Ukraine,
pr. Nauki 45, Kiev 03028, Ukraine

Received: October 6, 2004; In Final Form: December 1, 2004

The unusual green photoluminescence (PL) of *N*,*N*-dimethylformamide (DMF)/hydrochloric acid (HCl)/europium chloride ($EuCl_3$) solutions discovered earlier was investigated in more detail to clarify the emission mechanism. It was revealed that the DMF/HCl pair alone can yield a green PL band under UV excitation, and the emission has features of that of excimers. The addition of $EuCl_3$ salt to the solution further stimulates the green emission. The quantum yield of the line emission of Eu^{3+} ions at 592 and 612 nm is also affected by the presence of HCl in the solution. Both the green emission band and Eu^{3+} emission lines possess a common channel of excitation at ∼280 nm. This channel is the only source for the green emission band and an additional source for the Eu^{3+} emission lines, which can also be stimulated through a conventional Eu^{3+} excitation channel at 394 nm. The common excitation channel was found to be time-dependent, and its excitation maximum gradually shifts to longer wavelengths. Changes in the PL profiles of europium ions were also observed depending on the presence of HCl and the solution aging.

1. Introduction

Charge-transfer and energy-transfer interactions in molecular complexes with transition metal or lanthanide metal ions represent an interesting field of research. This interest is dictated by the actual and potential applications of the above complexes in photo- and electroluminescent devices,[1−3] solar cells,[4−6] sensory and diagnostic tools,[7−9] redox active catalysis for chemical reactions in coordination chemistry,[10,11] coatings against metal corrosion,[12−14] and so forth. One of the most interesting applications of the above complexes is in the field of light conversion, where the energy of light absorbed by a ligand can be transferred to the lanthanide ion which then emits light at a much longer wavelength.[1,15,16] Thus, the ligand assists the metal ion to emit high yield, because the absorption cross section of the lanthanide ion alone is small. On the other hand, there is a reverse influence of the metal ion on the photophysical properties of the ligand. The presence of a heavy ion in close vicinity to the ligand affects its singlet excited $\pi\pi^*$ state and facilitates population of the triplet state by intersystem crossing, thus leading to the effective phosphorescence of the ligand.[17−20] It is important also to note that tailoring of the organic ligand allows one to easily control the emission properties of the complex.[21]

Our interest is directed toward those charge-transfer (CT) complexes where an electron transfer can occur either between two organic molecules in the vicinity of a transition metal ion or directly between an organic ligand and a metal ion. In such a system, the metal possessing an alternating valence can serve as a charge trap or as an acceptor of the excited electron of the ligand. Charge trapping can result in drastic changes of the electrical[22] or photophysical[23] properties of the system.

Recently, we have discovered an unusual green emission of *N*,*N*-dimethylformamide (DMF) solutions of europium chloride ($EuCl_3$) in the presence of hydrochloric acid (HCl).[24] It has been proved that an electron transfer from the DMF/HCl environment to an Eu^{3+} ion takes place, because a divalent europium salt can be drawn out from the solution. Thus, the above emission was assigned to the divalent europium ions. However, further experiments have revealed a more pronounced role of the solvent in processes leading to the green emission. Herein, we report a more detailed investigation of the origin of the green emission band and the role of Eu^{3+} ions in processes of charge transfer and energy transfer responsible for the above phenomenon.

2. Experimental Section

DMF was distilled prior to use. Crystalline hydrate $EuCl_3{\cdot}6H_2O$ powder was dissolved in DMF to prepare a stock solution with a concentration of 10^{-1} M. This value was then varied by dilution with an additional amount of DMF to prepare solutions with desirable concentrations. Concentrated hydrochloride acid (37% aqueous solution) was used to prepare mixed DMF/HCl and DMF/$EuCl_3$/HCl solutions with the concentration of the HCl solution varied in the range 1−4 wt %.

Solution spectra were measured using a quartz cuvette. A xenon lamp was used to stimulate luminescence which was registered through a LOMO grating monochromator equipped with a photomultiplier tube counter, an amplitude discriminator, and a coincidence circuit. The final spectra were corrected for the spectral sensitivity of the registering system. Photoluminescence (PL) spectra from both the europium chloride, hydrochloride acid solutions and pure DMF were recorded in the same cuvette.

Spectral measurements of PL excitation were performed using the same light source. The excitation wavelength was scanned in the 250−450 nm range using a LOMO grating monochromator, while the emitted light passed through the analogous monochromator which was set at the required wavelength. The PL excitation spectra were corrected for the excitation lamp profile. PL emission and excitation spectra of $EuCl_3$ salt and HCl solutions in DMF were studied at various concentrations and aging times.

10.1021/jp045445e CCC: $30.25

Raman spectra of the solutions were measured using the same optical and registration equipment, while two lasers, a nitrogen laser with $\lambda_{exc} = 337$ nm or a copper laser with $\lambda_{exc} = 510$ nm, were employed as excitation sources.

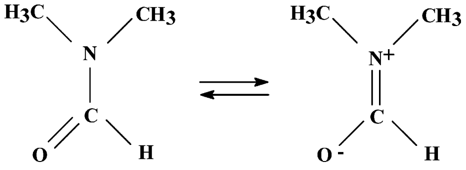
Electronic absorption spectra were recorded with a dual-beam SPECORD M40 spectrophotometer. The cuvette with pure DMF was used as a reference.

3. Results and Discussions

3.1. Green Emission of the DMF/HCl Solutions. Upon adding a small amount of concentrated HCl to DMF, appearance of the bright green emission from the DMF/HCl solution was found under UV excitation from the xenon lamp, with the PL maximum being at ~540 nm (Figure 1a). Upon further increase of the HCl concentration in DMF, the intensity of the green emission increased superlinearly. For example, a doubling of the HCl concentration in the solution from 1 to 2 wt % yielded a 4-fold increase of the PL intensity. Another factor leading to strengthening of the above emission was the solution aging. Upon storage of the solution under ambient conditions, the intensity of the green emission was found to increase, with a small shift of the emission maximum to 530 nm (Figure 1a, curve 4).

The PL excitation spectrum of the DMF/HCl solution showed a single band with the maximum at ~280 nm (Figure 1b). The intensity of this band also increased dramatically with a gradual increase of the acid concentration in the solution. The PL excitation maximum was found to shift considerably to longer wavelengths as a function of time until it reached its saturation value at ~312 nm (Figure 1b, curve 4).

There are several features of the green luminescence which are not typical of the conventional emission of organic chromophores in their monomer form. First, neither DMF nor HCl possesses any noticeable emission in the visible. We have reported earlier[24] that DMF possesses a wide smeared PL excitation band, probably due to the presence of intramolecular charge-transfer states, that is,



which are in dynamic equilibrium. The excitation band maximum is located in the 275−295 nm range depending on the registration wavelength of the emitted light. However, such an electronic excitation does not lead to the radiative recombination. The addition of HCl results in strengthening and narrowing of the excitation band, with appearance of the emission in the visible. Second, the above emission and excitation bands do not overlap and are separated far enough from each other. Third, the emission band is featureless; that is, it contains no vibrational overtones. Fourth, the emission band is very broad, with the full width at half-maximum (fwhm) being in the range 70−90 nm. The last three features are typical of the excimer emission.

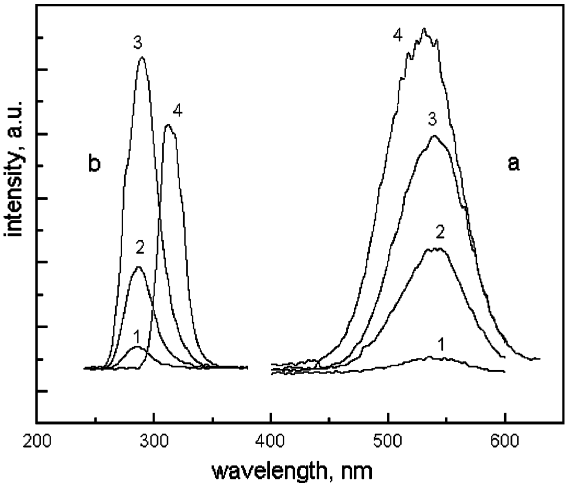
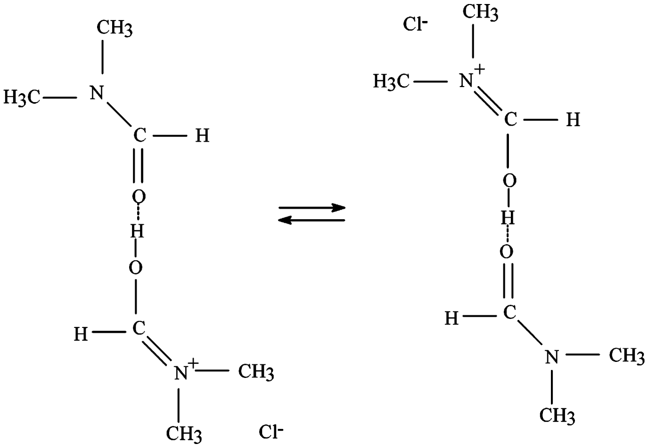


Figure 1. (a) PL emission ($\lambda_{exc} = 280$ nm) and (b) PL excitation ($\lambda_{reg} = 530$ nm) spectra of DMF/HCl mixtures with increasing concentration of HCl: (1) 1 wt %; (2) 2 wt %; (3) 3 wt %; (4) mixture 3 after 1 week ($\lambda_{exc} = 312$ nm, $\lambda_{reg} = 530$ nm).

As known, DMF is a weak base, where oxygen atoms of carbonyl groups serve as acceptors of protons.[25] The protonated carbonyl group is able to form a hydrogen bond with the neighboring DMF molecule. Thus, the excimer features observed in the spectra allow us to tentatively conclude that the green emission band originates from a dimer consisting of one excited DMF molecule and one neutral DMF molecule which are coupled together via a hydrogen bond and form the extended resonant forms, that is,



3.2. Effect of $EuCl_3$ on the Green Emission of DMF/HCl Solutions. It was found that a small addition of $EuCl_3$ to the DMF/HCl solution, with a salt concentration of $\sim 10^{-4}$ M or more, results in a noticeable increase of the green emission intensity (Figure 2a). However, this effect was moderate as compared with the effect of HCl. For example, a doubling of the $EuCl_3$ concentration from 1.5×10^{-4} to 3×10^{-4} M in DMF/HCl yielded an increase of the PL intensity by a factor of ~1.46. Further increase of the $EuCl_3$ concentration did not noticeably affect the intensity of the PL. However, the time factor did so significantly (Figure 2a, curve 4). On the other hand, the intensity of the PL excitation band monitored at $\lambda = 530$ nm was found to increase progressively with the increase of $EuCl_3$ concentration, simultaneously with the gradual shift of the band maximum to longer wavelengths (Figure 2b). Aging of the solution under ambient conditions resulted in a further shift of the excitation maximum to its limiting value at ~312 nm (Figure 2b, curve 4).

It has been found that the europium chloride is not a unique salt that facilitates the green emission of DMF solutions and that other trivalent metal ions, for example, La^{3+}, can also produce a similar effect. Crystalline hydrate $LaCl_3 \cdot 6H_2O$ powder was dissolved in DMF with a concentration of $\sim 10^{-1}$ M, and a green emission band with a maximum at 535 nm has been observed from the solution. In these experiments, however, a

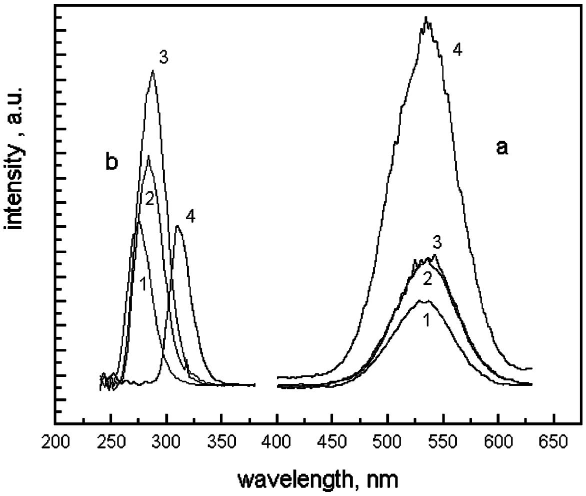


Figure 2. (a) PL emission (λ_{exc} = 280 nm) and (b) PL excitation (λ_{reg} = 530 nm) spectra of DMF/HCl/EuCl$_3$ mixtures with increasing concentration of EuCl$_3$: (1) no EuCl$_3$; (2) 1.5 × 10^{-4} M EuCl$_3$; (3) 3.0 × 10^{-4} M EuCl$_3$; (4) mixture 3 after 2 weeks (λ_{exc} = 312 nm, λ_{reg} = 530 nm). The concentration of HCl (2 wt %) is unchanged.

question still arises of whether the green PL is due to the direct effect of rare-earth cations or due to protons which might be produced as a result of the hydrolysis of a water residue present in DMF and/or salt. To answer this question, an aqueous solution of LaCl$_3$ of the same concentration (~10^{-1} M) has been prepared and its pH value was measured. The concentration of protons in such a solution resulting from water hydrolysis was ~10^{-4} M; this is 3 orders of magnitude lower than the concentration of protons in the DMFA/HCl mixture where a comparable green emission can be observed. Therefore, one can conclude that the trivalent metal ions produce some direct effect, because their production of protons is negligible.

It is known that rare-earth ions coordinate to the DMF molecule via an oxygen atom of the carbonyl group;[26] therefore, Eu^{3+} cations might serve as a bridge in forming the above extended resonant forms of neighboring DMF molecules. It should be noted, however, that a small amount of protons is still necessary to observe the green emission. For example, in the previous work,[24] the green emission was not observed from the as-prepared solutions of EuCl$_3$/DMF but was observed only from the solutions aged under ambient conditions, when water can be adsorbed from the atmosphere and then subjected to hydrolysis in the presence of salt in the solution. Thus, the question of whether the metal ions can be involved in the above process directly or serve as a sensitizer of the green emission is still debatable and requires additional experiments.

3.3. Effect of HCl on the Excitation and Emission Profiles of Eu^{3+} Ions in DMF. It was found that excitation and emission profiles of Eu^{3+} ions are strongly dependent on the solution conditions. The PL excitation spectra revealed a considerable discrepancy with the electronic absorption spectra. First, the PL excitation spectra of DMF/EuCl$_3$ solutions, monitored at λ_{reg} = 613 nm, showed two major excitation maximums, located at 318 and 394 nm, respectively (Figure 3). Although these maximums are consistent with the $^7F_0 \rightarrow {}^5H_6$ and $^7F_0 \rightarrow {}^5L_6$ electronic transitions in the Eu^{3+} ion, respectively,[27] these electronic transitions have been revealed not as narrow lines but as broadened bands in the excitation spectra versus narrow lines in the electronic absorption spectra (see Table 1 and Figure 3). Both excitation bands were broadened asymmetrically to the short-wave region. As can be seen from Figure 3, several excitation levels become broadened and merge into one continuous band. Such a broadening can be explained by splitting of the major levels of Eu^{3+} due to electric fields of the DMF ligand formed. However, it is known that in crystals a similar effect is restricted by splitting no more than 500 cm^{-1},[27] while the above broadening is more pronounced (Table 1). The previous experiments[24] have shown that the charge-transfer (CT) process in Eu^{3+}/DMF yields relatively long-lived states of the divalent europium which can be drawn out from the solution. Thus, the anomalous broadening of the PL excitation bands of Eu^{3+}/DMF can be explained by contribution of the CT states to the excitation spectra. In this sense, the excited europium ions in DMF should be presented as a superposition of their trivalent and divalent states.

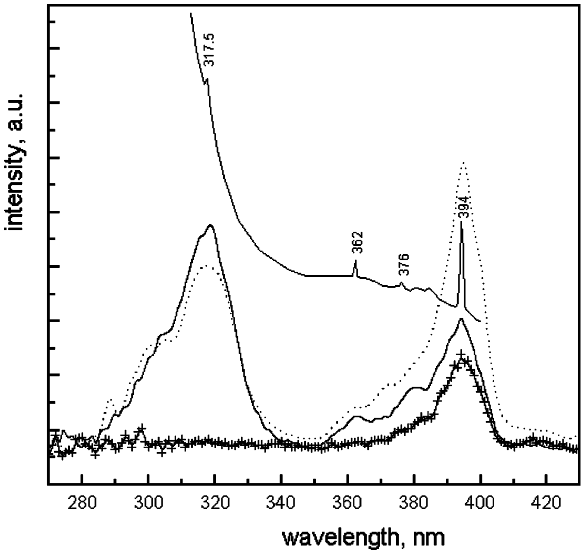


Figure 3. PL excitation spectra of DMF/EuCl$_3$ solutions (salt concentration is 1.5 × 10^{-2} M, λ_{reg} = 613 nm): (dotted curve) no HCl; (crosses) excess of HCl (7 wt %). Spectra of PL excitation at λ_{reg} = 618 nm of the solution with 1 wt % HCl (lower solid curve) and electronic absorption of DMF/EuCl$_3$ (upper solid curve) are shown for comparison. The electronic absorption spectrum is corrected for the absorption of DMF.

TABLE 1: fwhm (cm^{-1}) of the Excitation Band at 394 nm in DMF/HCl/EuCl$_3$ Mixtures

as-prepared DMF/EuCl$_3$ mixture (no HCl)	as-prepared DMF/EuCl$_3$ + HCl (1 wt %)	aged DMF/EuCl$_3$ + HCl (1 wt %)	DMF/EuCl$_3$ with excess HCl (7 wt %)
1030	1481	1610	1160

Second, the addition of a small amount of HCl (~1 wt %) has resulted in a further increase of the fwhm of the above excitation bands (Table 1), with the clear evidence of complex structure of these bands, as can be seen from an additional maximum at 304 nm (Figure 4). Solution aging led to redistribution of the excitation intensities in favor of the long-wave band at 394 nm. Meanwhile, acid addition resulted in the appearance of the green PL, whose excitation band, monitored at λ_{reg} = 540 nm, also increased with time. It is interesting that the above temporal changes of profiles of the excitation bands responsible for the green emission band and red emission lines possess a common isosbestic point at ~350 nm (Figure 4). This result points out that there is energy transfer from one excitation channel to the other, which influences intensity redistribution of the band and line emissions under the common excitation wavelength λ_{exc} = 318 nm (Figure 5).

It was found that the successive addition of HCl (a few weight percents) to the EuCl$_3$/DMF solution, with the EuCl$_3$ concentration in the range ~10^{-3}–10^{-2} M, normally suppresses the

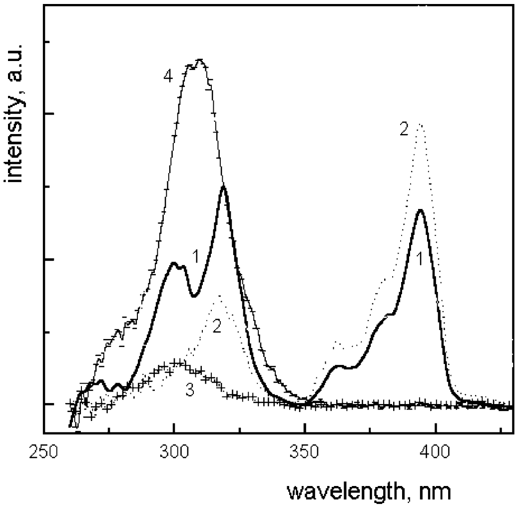


Figure 4. PL excitation spectra of the DMF/EuCl$_3$/HCl mixture monitored at $\lambda_{reg} = 613$ nm (1, as-prepared mixture; 2, the same mixture 3 days later) and $\lambda_{reg} = 540$ nm (3, as-prepared mixture; 4, the same mixture 3 days later). The concentration of EuCl$_3$ is 1.5×10^{-2} M, and the concentration of HCl is 1 wt %.

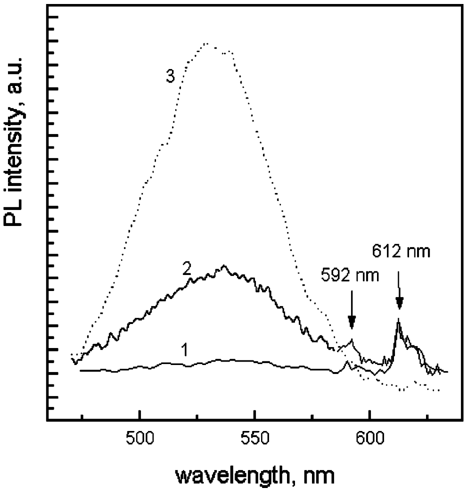


Figure 5. PL emission spectra of the DMF/HCl/EuCl$_3$ mixture: (1) as-prepared mixture, $\lambda_{exc} = 280$ nm; (2) mixture 1 after 3 days, $\lambda_{exc} = 318$ nm; (3) mixture 2 after doubling of the concentration of HCl. The initial concentration of HCl is 1 wt %, and the concentration of EuCl$_3$ is 1.5×10^{-2} M.

intensity of the line emission of Eu^{3+} ions in the red part of the spectrum. As has been shown above, the Eu^{3+} line emission has two major excitation bands in different parts of the PL excitation spectrum, namely, at ~318 and 394 nm. The effect of suppression of the emission lines on acid adding was not dependent on whether the PL lines were excited under 318 or 394 nm excitation wavelengths. When using the 318 nm excitation wavelength, acid addition yielded an increase of only the green emission band (Figure 5, curve 3). Therefore, redistribution of the excitation efficiency within the common excitation channel in favor of the band emission can be concluded. The line emission can be suppressed both by HCl addition and as a result of aging of the solution mixture. Both factors also lead to the suppressed line emission which is stimulated by the excitation wavelength at 394 nm (Figure 6); however, a complete suppression of the emission lines stimulated by this excitation wavelength was not observable, in contrast to the complete suppression of the emission lines stimulated by the excitation wavelength at 318 nm (Figure 5).

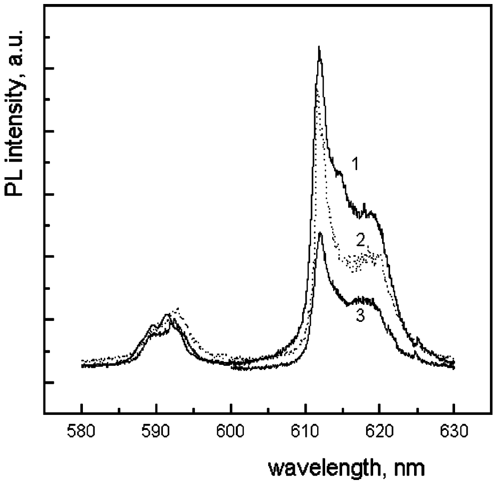


Figure 6. PL emission spectra of the DMF/EuCl$_3$ (1.5×10^{-2} M) solution ($\lambda_{exc} = 394$ nm): (1) as-prepared; (2) after the addition of HCl (1 wt %); (3) mixture 2 after 3 days.

TABLE 2: Intensity Ratio $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ of the Emission Lines at 612 and 590 nm as Excited by Different Wavelengths

excitation wavelength	318 nm	360 nm	380 nm	394 nm
intensity ratio	1.20−1.40	1.38	1.73	2.35

The profile of the Eu^{3+} line emission at 591.5 and 611.8 nm, which correspond to the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ electronic transitions, respectively,[27] was found to be also affected by the presence of HCl in the solution (Figure 6). Upon adding the acid, the first maximum becomes shifted to ~592.4 nm, while the second maximum does not shift. The profiles of both lines change and show a fine structure, that is, additional lines at 589.9 and 618.0 nm which become more pronounced with the acid concentration increase and solution aging (Figure 6). The changes also show a decrease of a shoulder contribution at 615 nm, while the relative contribution of the emission line at 618 nm increases, and the intensity ratio of 612 to 618 nm lines becomes reduced. Changes in the fine structure of the emission profiles point out the changed local symmetry of the europium ion environment.

Finally, it should be noted that an excess of HCl (~5−10 wt %) in the EuCl$_3$/DMF solution leads to the complete suppression of the 318 nm band and narrowing of the 394 nm band, respectively, in the PL excitation spectrum (Figure 3 and Table 1). These changes can also be explained by the change in local symmetry of the europium ions. The reduced width of the latter band and disappearance of its fine structure points out that the local symmetry increases. That is probably due to the increase of the number of chlorine anions which coordinate to the Eu^{3+} ion.

The addition of HCl to the solution also resulted in changes of the intensity ratio of the emission lines at 612 and 590 nm. This ratio decreases with increasing HCl, and the intensity of the emission at 612 nm is more affected by the presence of HCl as compared with the emission at 590 nm (Figure 6). A similar change can be observed when tuning the excitation wavelength from 394 to 318 nm (Table 2). That means that the electronic transition leading to the emission at 590 nm borrows energy more effectively from the additional excitation sources as compared with the electronic transition leading to the emission at 612 nm. The same effect of HCl, as was mentioned, was observed in respect to the intensity ratio of the emission lines at 612 and 618 nm. The latter electronic transition seems to borrow energy both from the excitation channel at 394 nm

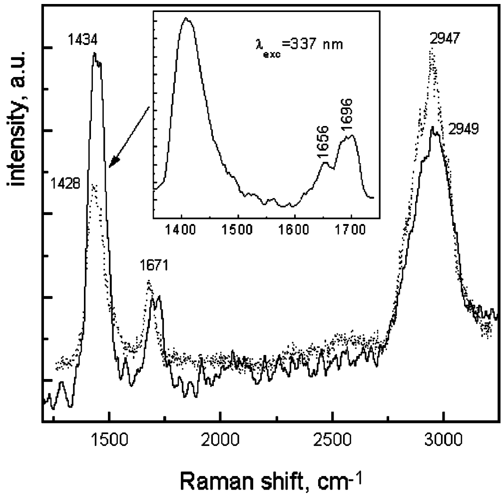


Figure 7. Raman spectra of the DMF/HCl solution. The excitation wavelengths are 337 nm (solid curve) and 510 nm (dotted curve). The inset shows details of the fine structure.

and from the excitation channel at 318 nm with equal efficiency, as can be concluded from Figure 3.

3.4. Resonance Raman Scattering. Irradiation of the EuCl$_3$/HCl/DMF mixture by light with the wavelength leading to the green emission also leads to the resonance Raman scattering by those vibrational modes which interact with the radiative electronic transition. A nitrogen laser is applicable for that experiment because its wavelength ($\lambda = 337$ nm) is still within the wide excitation band responsible for the green emission.

Raman spectra of the DMF/HCl solution showed three major bands at ~1432, 1675, and 2948 cm^{-1} (Figure 7) which correspond to the symmetric CH$_3$ bending, carbonyl C=O stretching, and asymmetric CH$_3$ stretching vibrations of the DMF molecule, respectively.[28] It should be noted that the DMF molecule does not possess a point of symmetry, so the lack of the inversion point leads to the nonexclusion of Raman and IR active modes. The carbonyl vibration band was sensitive to the excitation wavelength that probes the solution. Upon using the excitation wavelength at 510 nm, this band showed a quite symmetric profile, with the maximum at 1671 cm^{-1}, whereas the use of the excitation wavelength at 337 nm showed the blue shift of this band to ~1700 cm^{-1} (Figure 7). The band at 1432 cm^{-1} was also affected by the excitation wavelength, and a relative contribution of this band increased as compared with the other bands when using the excitation wavelength of the nitrogen laser. The addition of EuCl$_3$ salt to DMF that stimulates its green emission further affected the carbonyl vibrational mode and resulted in its gradual shift to ~1730 cm^{-1} and its intensity increase with the salt concentration increase (Figure 8). A detailed study revealed splitting of this band into two components (inset in Figure 7), one of which was equivalent to that observed when using the excitation wavelength 510 nm and the other component was blue shifted. The latter component is believed to be due to the resonance Raman scattering of those DMF molecules which interact with HCl. The resonance Raman spectra confirm the conclusion that the carbonyl group of DMF is involved in the electronic process leading to the green emission, as shown in the scheme of the extended resonant forms above.

4. Conclusions

The analysis of the above results shows that electronic processes leading to the green emission originate from DMF, rather than the divalent europium ion, as was proposed in the previous work.[24] It has been found that the green emission can be induced only by the addition of a small amount of hydrochloric acid to DMF, without any other emitting ions in the solution. The green emission has several features which are attributable to the excimer emission, such as large separation of the emission and excitation wavelengths, a very broad and unstructured emission band profile. An interesting feature is that the PL excitation profile responsible for the green emission is time-dependent. These features lead to the conclusion that the green emission comes from the dimerization of DMF molecules in the acidic environment, a process which is unstable and time-dependent. The role of trivalent metal ions in the above process may also be significant. However, the question of whether the metal ion functions directly in the above process or serves as an indirect sensitizer of the green emission is still debatable and requires additional experiments.

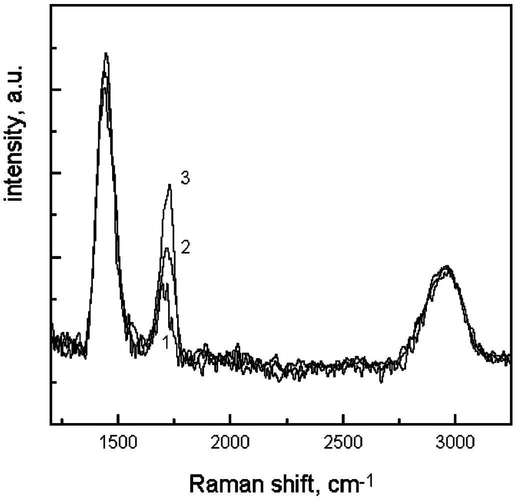


Figure 8. Raman spectra of the DMF/EuCl$_3$ solution with increasing concentration of EuCl$_3$: (1) 4×10^{-4} M EuCl$_3$; (2) 3×10^{-3} M EuCl$_3$; (3) 1×10^{-2} M EuCl$_3$. The excitation wavelength is 337 nm.

It has been found that the green emission band of DMF/HCl at 540 nm and Eu^{3+} emission lines at 590 and 612 nm possess a common excitation channel in the 280–318 nm region, which makes it possible to use Eu^{3+} ions as a probe to control energy transfer in electronic processes responsible for the green emission. The above experiments have shown that the addition of HCl and/or solution aging causes the energy transfer in favor of the band emission when using the common excitation wavelength. The presence of HCl also leads to the increased contribution of CT states to the excitation of Eu^{3+} ions and to the changes in the fine structure of their emission profiles. These changes confirm the redistribution in local environment of the europium ion that accompanies the green luminescence of the DMF/HCl/EuCl$_3$ system.

Acknowledgment. We thank Dr. A. Pud from Institute of Bioorganic Chemistry and Petrochemistry for his help with the purification of the solvent and valuable discussions. We also appreciate a suggestion of the anonymous referee on how to improve the manuscript.

References and Notes

(1) Bekiari, V.; Lianos, P. *J. Lumin.* **2003**, *101*, 135.

(2) Capecchi, S.; Renault, O.; Moon, D.-G.; Halim, M.; Etchells, M.; Dobson, P. J.; Salata, O. V.; Christou, V. *Adv. Mater.* **2000**, *12*, 1569.

(3) Yu, G.; Liu, Y.; Wu, X.; Zhu, D.; Li, H.; Jin, L.; Wang, M. *Chem Mater.* **2000**, *12*, 2537.

(4) Kawano, K.; Arai, K.; Yamada, H.; Hashimoto, N.; Nakata, R. *Sol. Energy Mater. Sol. Cells* **1997**, *48*, 35.

(5) Mashida, K.; Li, H.; Ueda, D.; Inoue, S.; Adachi, G. *J. Lumin.* **2000**, *87*, 1257.

(6) De Sa, G. F.; Malta, O. L.; De Mello Donega, C.; Simas, A. M.; Longo, R. L.; Santa Cruz, P. A.; Da Silva, E. F., Jr. *Coord. Chem. Rev.* **2000**, *196*, 165.

(7) Yam, V. W.-W.; Lo, K. K.-W. *Coord. Chem. Rev.* **1999**, *184*, 157.

(8) Keefe, M. H.; Benkstein, K. D.; Hupp, J. T. *Coord. Chem. Rev.* **2000**, *205*, 201.

(9) Valeur, B.; Leray, I. *Coord. Chem. Rev.* **2000**, *205*, 3.

(10) Higuchi, M.; Ikeda, I.; Hirao, T. *J. Org. Chem.* **1997**, *62*, 1072.

(11) Hirao, T. *Coord. Chem. Rev.* **2002**, *246*, 81.

(12) Epstein, A. J.; Smallfield, A. O.; Guan, H.; Fahlman, M. *Synth. Met.* **1999**, *102*, 1374.

(13) Fahlman, M.; Crispin, X.; Guan, H.; Li, S.; Smallfield, A. O.; Wei, Y.; Epstein, A. J. *Polym. Prepr*. **2000**, *41*, 1753.

(14) Posdorfer, J.; Wessling, B. *Synth. Met*. **2001**, *119*, 363.

(15) Weissman, S. I. *J. Chem. Phys.* **1942**, *10*, 214.

(16) Sabbatini, N.; Guardigli, M.; Lehn, J.-M. *Coord. Chem. Rev.* **1993**, *123*, 201.

(17) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. F. *Nature* **1998**, *395*, 151.

(18) O'Brien, D. F.; Baldo, M. A.; Thompson, M. E.; Forrest, S. F. *Appl. Phys. Lett.* **1999**, *74*, 442.

(19) Baldo, M. A.; Lamansky, S.; Burrows, P. E.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **1999**, *75*, 4.

(20) Kwong, R. C.; Sibley, S.; Dubovoy, T.; Baldo, M. A.; Forrest, S. R.; Thompson, M. E. *Chem. Mater.* **1999**, *11*, 3709.

(21) Bekiari, V.; Lianos, P. *Adv. Mater.* **2000**, *12*, 1603.

(22) Dimitriev, O. P.; Kislyuk, V. V. *Synth. Met.* **2002**, *132*, 87.

(23) Wang, X.-Y.; Del Guerzo, A.; Schmehl, R. H. *J. Photochem. Photobiol., C* **2004**, *5*, 55.

(24) Dimitriev, O. P.; Kislyuk, V. V. *Chem. Phys. Lett.* **2003**, *377*, 149.

(25) Fraenkel, G.; Franconi, C. *J. Am. Chem. Soc.* **1960**, *82*, 4478.

(26) Krishnamurthy, S. S.; Saundararajan, S. *J. Inorg. Nucl. Chem.* **1966**, *28*, 1689.

(27) Poluektov, N. S.; Kononenko, L. I.; Efryushina, N. P.; Beltyukova, S. V. *Spectrophotometry and luminescent techniques of probing rare-earth elements*; Naukova Dumka: Kiev, Ukraine, 1989; p 255.

(28) Varfolomeev, M. B.; Kravchenko, V. V.; Mayants, A. L.; Petrov, V. E.; Plyuschev, V. E.; Petrov, K. I. *Russ. J. Inorg. Chem.* **1973**, *18*, 669.