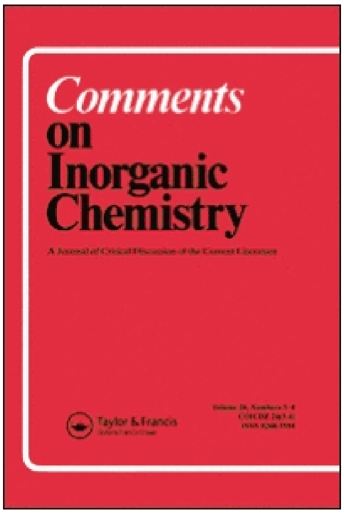

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The Luminescence Rigidochromic Effect Exhibited by Organometallic Complexes: Rationale and Applications

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The Luminescence Rigidochromic Effect Exhibited by Organometallic Complexes: Rationale and Applications

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Several transition-metal organometallic complexes exhibit an especially pronounced hypsochromic shift of their luminescence bands when their solution environment becomes more rigid. This unusual spectroscopic effect has been termed "luminescence rigidochromism" and is apparently confined to metal-to-ligand charge-transfer excited states. Attention is drawn here to the types and photophysical characteristics of organometallic complexes that demonstrate this phenomenon and its underlying causes. Recently, a number of practical applications have arisen based on the luminescence rigidochromic effect; these involve a variety of material processes, including thermal and photochemical polymerizations and the sol-gel process. In each case an organometallic complex has been incorporated as a spectroscopic probe to monitor the large environmental changes that occur.

Key Words: *luminescence spectroscopy, emission spectroscopy, photophysical processes, electronically excited states, electronic spectroscopy, metal complexes, charge-transfer, polymers, photopolymers, polymerization, thin films, curing, sol-gel*

Abbreviations: py = pyridine, 4-ACpy = 4-acetylpyridine, 4-BNpy = 4-benzoylpyridine, 4-CNpy = 4-cyanopyridine, 4-FMpy = 4-formylpyridine, 3-BNpy = 3-benzo-

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ylpyridine, 4-BNpy = 4-benzoylpyridine, 4-Phpy = 4-phenylpyridine, pip = piperidine, pyz = pyrazine, bpy = 2,2'-bipyridine, 4,4'-bpy = 4,4'-bipyridine, phen = 1,10-phenanthroline, 4-Me-phen = 4-methyl-1,10-phenanthroline, 5-Me-phen = 5-methyl-1,10-phenanthroline, 5-Br-phen = 5-bromo-1,10-phenanthroline, 5-Cl-phen = 5-chloro-1,10-phenanthroline, 5-NO_2-phen = 5-nitro-1,10-phenanthroline, 4,7-Ph_2-phen = 4,7-diphenyl-1,10-phenanthroline, 4,4'-Me_2-phen = 4,4'-dimethyl-1,10-phenanthroline, phen-5,6-dione = 1,10-phenanthroline-5,6-dione, en = ethylenediamine, biquin = 2,2'-biquinoline, bpe = trans-1,2-bis(4-pyridyl)ethylene, bpa = 1,2-bis(4-pyridyl)ethane, Cp = η^5-C_5H_5, EPA = 5:5:2 ether-isopentane-ethanol, MCH = methylcyclohexane, DGEBA = diglycidyl ether of bisphenol A, TMPTA = trimethylolpropane triacrylate, PMMA = poly(methyl methacrylate), MLCT = metal-to-ligand change-transfer, LF = ligand field, IL = intraligand, RR = resonance Raman, ϕ_e = emission quantum yield, τ_e = emission lifetime, k_r = radiative rate constant, k_{nr} = nonradiative rate constant, η^* = complex viscosity.

INTRODUCTION

One of the most interesting, and yet rather overlooked, features of the luminescence properties displayed by transition-metal organometallic complexes is the manner in which charge-transfer emission bands undergo large hypsochromic shifts when the supporting environment becomes rigid.[1] This effect has been referred[2] to as "luminescence rigidochromism" and, despite the fact that it was recognized over 20 years ago, its exact causes are only now becoming apparent.

Understanding this phenomenon is not only necessary to further our knowledge of organometallic photophysical processes, but it has increased in significance, as it appears that this unusual spectroscopic behavior may give rise to some very useful industrial applications. The purpose of this article is to focus on the characteristics of the luminescence rigidochromic effect, to recognize the types of metal complexes that exhibit it, to explore the underlying reasons for its existence, and to draw attention to some of the practical applications that are emerging from it.

COMPLEXES EXHIBITING LUMINESCENCE RIGIDOCHROMISM

The first observation and reference to luminescence rigidochromism appeared in 1974 for a series of *fac*-$ClRe(CO)_3L$ (L = bpy, phen, 5-Me-phen, 5-Br-phen, 5-Cl-phen, 5-NO_2-phen, 4,7-Ph_2-phen, phen-

5,6-dione and biquin) complexes.[2] These metal carbonyl species are actually among the strongest emitters known, and their lowest energy excited states yield readily detectable emission in the visible region from a variety of environments, including fluid solution.[1,2] The *fac*-$ClRe(CO)_3L$ compounds are also representative of a much larger series of organometallic compounds where the unique ligand (usually an α,α'-diimine or pyridine group) possesses a low-lying empty π^*-acceptor orbital. Such complexes typically give rise to intense lowest energy metal-to-ligand charge-transfer (MLCT) absorption bands, and it is these excited states which are responsible for the luminescence.[1] Indeed, in *fac*-$XRe(CO)_3(bpy)$ (X = Cl or Br) time-resolved resonance Raman (RR) spectral measurements strongly support this Re → π^*(bpy) MLCT assignment, and excited-state Raman lines have been observed that are attributable to the bpy radical anion.[3]

Table I summarizes the luminescence characteristics and environmental effects determined from a series of *fac*-$ClRe(CO)_3L$ complexes. The emission quantum yields (ϕ_e) illustrate that the radiative decay pathways are favored when the temperature is reduced from 298 to 77 K and the solution becomes frozen. The emission lifetimes (τ^e) reveal that the emitting states are relatively long lived, being on the order of hundreds of ns in benzene solution and several μs in EPA at 77 K. However, it is the shift in energy of the emission

TABLE I

Luminescence properties of *fac*-$ClRe(CO)_3L$ complexes[a]

L	Emission Max, 10^{-3}cm^{-1}		τ_e μs		ϕ_e (±15%)[c]	ϕ_e (±15%),
	298 K	77 K	298 K	77 K	298 K	77 K
phen	17.33	18.94	0.3	9.6	0.036	0.33
bpy		18.87	0.6	3.8		
5-Me-phen	17.01	18.83	<0.65	5.0	0.030	0.30
4,7-Ph_2-phen	17.24	18.18	0.4	11.25		
5-Cl-phen	17.12	18.69	<0.65	6.25		
5-Br-phen	17.12	18.69	<0.65	7.6	0.020	0.20
5-NO_2-phen	*b*	18.28		11.8		0.033
phen-5,6-dione	*b*	18.45		2.5		
biquin[c]	*b*	14.58				

[a]Data taken from Ref. 2. Measurements in EPA at 77 K or in CH_2Cl_2 at 298 K.
[b]Luminescene was not detectable from these complexes in solution at 298 K.
[c]Quantum yields determined in benzene at 298 K.

maximum on cooling to 77 K that is so unusual and a clear indication of luminescence rigidochromism. This is further illustrated by Fig. 1 which depicts electronic absorption and emission spectra obtained from a representative complex, *fac*-ClRe(CO)$_3$(phen), in EPA at 298 and 77 K. Although there is a relatively small shift in the energy of the lowest MLCT absorption band on cooling, the emission band is much more substantially moved.

Whereas the heavy metal in these organometallic complexes precludes a pure multiplicity description of the lowest lying MLCT excited states,[4] there is now considerable evidence to support the notion that the emitting levels are of predominantly triplet character.[1] For instance, the emission from *fac*-ClRe(CO)$_3$(phen) is known to be quenched by the triplet energy levels of anthracene (E_T = 14,700 cm^{-1})[5] and *trans*-stilbene (E_T = 17,500 cm^{-1})[6]; in each instance, the energy transfer obeys Stern–Volmer kinetics. In the case of the

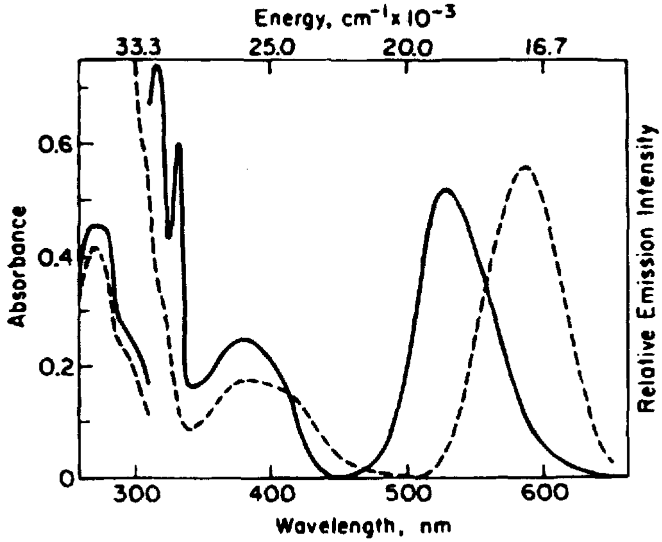


FIGURE 1 Electronic absorption (left) and emission (right) spectra of *fac*-ClRe(CO)$_3$-(phen) in EPA at 77 K (—) and 298 K (---). Room temperature absorption maxima are at 26,100 cm^{-1} (ϵ = 4000) and 37,030 cm^{-1} (ϵ = 30,600). The low-temperature spectrum is uncorrected for solvent contraction, and the emissions at 77 and 298 K were not recorded at the same sensitivity. Data taken from Ref. 2.

quenching by stilbene, a *trans* → *cis* isomerization of stilbene takes place, further implying that it is the triplet excited state of *trans*-stilbene that is involved in the energy transfer mechanism.[7] Moreover, the *trans* → *cis* isomerization yields for the stilbene are observed to be the same, within experimental error, as those obtained in the benzophenone sensitization of *trans*-stilbene,[6] suggesting that the intersystem crossing efficiency is unity in the *fac*-$ClRe(CO)_3L$ system.[8] Consequently, the above spectral data indicate that the rigidochromic effect is exhibited mainly by the triplet-centered emitting MLCT states and to a much lesser extent by the singlet MLCT absorptions.

It is important to stress that the luminescence rigidochromism is associated with the change in the rigidity of the medium and it is not a temperature effect. This is clearly illustrated by results obtained on the *fac*-$ClRe(CO)_3L$ system in a wider variety of environments (see Table II).[2] For each complex it can be seen that the emission

TABLE II

Environmental effects on MLCT absorption and emission maxima of *fac*-$ClRe(CO)_3L$ complexes[a]

L	Environment	Absorption Max, 10^{-3} cm^{-1}	Emission Max, 10^{-3} cm^{-1} (τ_e μs)
phen	CH_2Cl_2, 298 K	26.53	17.33 (0.3)
	polyester resin, 298 K		18.52 (3.67)
	EPA, 77 K		18.94 (9.6)
5-Me-phen	benzene, 298 K	25.65	17.00 ($\leq$ 0.65)
	CH_2Cl_2, 298 K	26.32	17.01
	CH_3OH, 298 K	27.05	17.00
	pure solid, 298 K		18.42
	polyester resin, 298 K		18.48 (3.5)
	EPA, 77 K		18.83 (5.0)
5-Br-phen	benzene, 298 K	25.32	17.15 ($\leq$ 0.65)
	CH_2Cl_2, 298 K	25.84	17.12
	CH_3OH, 298 K	26.88	17.04
	pure solid, 298 K		17.83
	polyester resin, 298 K		18.32 (2.2)
	EPA, 77 K		18.69 (7.6)
5-Cl-phen	CH_2Cl_2, 298 K	25.91	17.12
	pure solid, 298 K		17.99
	EPA, 77 K		18.69 (6.25)

[a] Data taken from Ref. 2.

maxima are subjected to quite substantial hypsochromic shifts (up to 1,883 cm^{-1}) as the medium becomes rigid. Typically, under fluid solution conditions a red-orange emission is detected which turns yellow-green in a rigid environment. Significantly, these energy shifts are observed to take place at room temperature if the complex is supported in a rigid polyester resin.

Analogous observations have been made from a series of luminescent $W(CO)_5L$ (L = 4-ACpy, 4-BNpy, 4-CNpy and 4-FMpy) complexes (see Fig. 2).[9] In each case the emission band has been associated with the ^{3}MLCT states and appears at significantly higher energies from the solid compounds than in solution. Detailed photophysical studies have revealed the effect of different environments

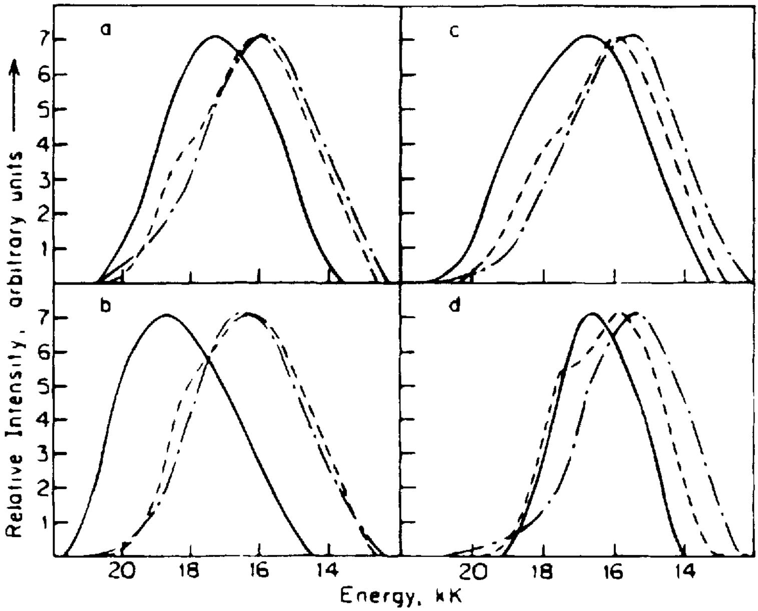


FIGURE 2 Emission spectra at 298 K of (a) $W(CO)_5(4\text{-ACpy})$, (b) $W(CO)_5(4\text{-BNpy})$, (c) $W(CO)_5(4\text{-CNpy})$, and (d) $W(CO)_5(4\text{-FMpy})$; (—) solid, (---) 6–8 × 10^{-5} M $W(CO)_5L$ in methylcyclohexane and (-·-) 4–6 × 10^{-5} M $W(CO)_5L$ in benzene. Excitation wavelength is 400 nm. Spectra were corrected for wavelength variations in detector response; intensities are scaled to make maxima equal. Data taken from Ref. 9a.

on the molecular photophysics of the $W(CO)_5$(4-CNpy) and $W(CO)_5$(pip) derivatives (see Table III).[9b] The long wavelength MLCT emission from $W(CO)_5$(4-CNpy) is observed as two features in 296 K EPA (20,325 and 15,385–16,667 cm^{-1}) and these move to higher energy on cooling to 77 K (20,450 and 16,863 cm^{-1}); the lowest emission band, in particular, showing a substantial rigidochromic shift. The absorption and photophysical data obtained from $W(CO)_5$(pip) are included for comparison; they indicate the positions of the higher energy ligand field (LF) bands which do not display the luminescence rigidochromic effect.

The $M(CO)_4L$ (M = Mo or W, L = 4-Me-phen, 5-Me-phen, 4,7-Ph_2-phen) system represents another dual MLCT emission system that has been found to exhibit luminescence rigidochromism.[10,11] Table IV summarizes the effects of changing the solution environment and rigidity on the energies of both of the emission bands.[10b] Again, it is the lowest energy transition that is significantly blue shifted. Previously, following detailed studies of the electronic structure of these $M(CO)_4L$ complexes, it has been determined that the low-energy MLCT absorption actually consists of three MLCT transitions; the most intense band being attributed to a z-polarized (d_{yz}) $b_2 \rightarrow b_2$ (π^*) transition that is directed along the dipole vector of the complex.[12] The extent of solvent dependence for a wide range of these complexes can be correlated with the mixing of the metal d_{yz} and ligand π^* orbitals. It has been observed that an increased mixing lowers the MLCT character and, hence, the solvent sensitivity of the $b_2 \rightarrow b_2$ (π^*) transition.[12c] In the case of the substituted phen complexes the amount of orbital mixing is found to be quite small, and indeed the complexes are extremely solvatochromic.[10,11f,12c,13] Other y-polarized ($d_{x^2-z^2}$) $a_1 \rightarrow b_2$ (π^*) and x-polarized (d_{xy}) $a_2 \rightarrow b_2$ (π^*) MLCT components have been identified in RR excitation profiles of the $M(CO)_4L$ system.[12c]

Both emission bands of the $M(CO)_4L$ complexes are solvent sensitive and believed to contain ^{3}MLCT character.[10b] The lowest energy feature undergoes a substantial rigidochromic effect as noted by comparing the data in EPA at 293 and 80 K (see Table IV). This band is understood to comprise the above $b_2 \rightarrow b_2$ (π^*), $a_1 \rightarrow b_2$ (π^*) and $a_2 \rightarrow b_2$ (π^*) MLCT transitions on the basis of the RR results and excitation spectra.[10b,12c] On the other hand, the higher

TABLE III

Environmental effects on absorption, emission and excitation maxima and emission lifetimes for $W(CO)_5$(4-CNpy) and $W(CO)_5$(pip)[a]

				Emission	
Complex	Environment	Abs λ_{max}, nm	Exc λ_{max}, nm	λ_{max}, nm	τ_e, μs
$W(CO)_5$(4-CNpy)	MCH, 296 K	335, 371 (sh), 404, 454, 495 (sh)	371 (sh), 405, 460, 505 (sh)	545	0.292
			371 (sh), 405, 460, 505 (sh)	613	0.292
	EPA, 296 K	365 (sh), 402, 436	*b*	492	*b*
			b	600–650 (br)	*b*
	EPA, 77 K	322, 381, 423	343, 367, 403	489	11.4
			371, 397, 400	593	20.1
$W(CO)_5$(pip)	MCH, 296 K	384 (sh), 405, 450 (sh)		*c*	
	EPA, 77 K	378 (sh), 400, 441 (sh)	373, 397, 445	532	4.7

[a] Data taken from Ref. 9b. Emission spectra recorded following excitation at 400 nm; lifetimes and excitation data obtained at the corresponding emission maxima; sh = shoulder; br = broad.

[b] Emission only weakly observed, and excitation data and lifetime not obtained.

[c] No emission observed.

TABLE IV

Emission maxima of $M(CO)_4(\alpha,\alpha'\text{-diimine})$ complexes in various solutions[a]

Complex	λ_{em}, nm Benzene, 293 K	 EPA, 293 K	 EPA, 80 K
$Mo(CO)_4$(4-Me-phen)	546,752	553,765	533,647
$Mo(CO)_4$(5-Me-phen)	568,764	572,772	530,658
$Mo(CO)_4$(4,7-Ph_2-phen)	582,770	585,785	545 (sh), 660
$Mo(CO)_4$(en)	*b*	*b*	*b*
$W(CO)_4$(4-Me-phen)	585,782	584, > 780	527,677
$W(CO)_4$(4,7-Ph_2-phen)	595,780	595, > 800	550 (sh), 675
$W(CO)_4$(en)	*b*	*b*	542

[a] Data taken from Ref. 10b. Excitation wavelength is 400 nm, and the spectra are fully corrected for wavelength variations in detector response; sh = shoulder.
[b] No emission observed.

energy emission is considerably less solvent dependent and exhibits less rigidochromism. This band is understood to comprise emission from $a_2 \rightarrow a_2$ (π^*) MLCT and LF states; the latter level is known to be emissive at low temperature and its position is virtually isoenergetic to the ^{3}MLCT emission, as illustrated by data from $W(CO)_4$en.[10b] The ^{3}LF emission clearly interferes with the upper ^{3}MLCT emission at 80 K, and this likely contributes to the reduced luminescence rigidochromism of the higher energy band.

Emission studies on a series of *fac*-$XRe(CO)_3L^+$ (X = CH_3CN, PhCN, py or pip, L = phen or biquin) complexes have revealed a further aspect of luminescence rigidochromism. These molecules exhibit multiple emissions from Re → π^*(phen) and intraligand (IL) excited states. Figure 3 depicts emission spectra obtained from *fac*-$[(CH_3CN)Re(CO)_3(phen)](CF_3SO_3)$ in EPA at 298 and 77 K.[14] Use of a phosphoroscope permits detection of the longer-lived (>50 μs) ^{3}IL component (τ_e = 75 μs at 77 K) and not the ^{3}MLCT emission (τ_e = 11 μs at 298 K). This result demonstrates that the ^{3}MLCT emission is subjected to a considerable energy shift, whereas the ^{3}IL emission is not. Clearly, the luminescence rigidochromism is associated only with the ^{3}MLCT states and not the ^{3}IL levels.

Finally, there are several other systems that exhibit significant shifts in their emission bands on forming a frozen glass at low temperature. Among these include a series of bridged $(OC)_5W$-L-

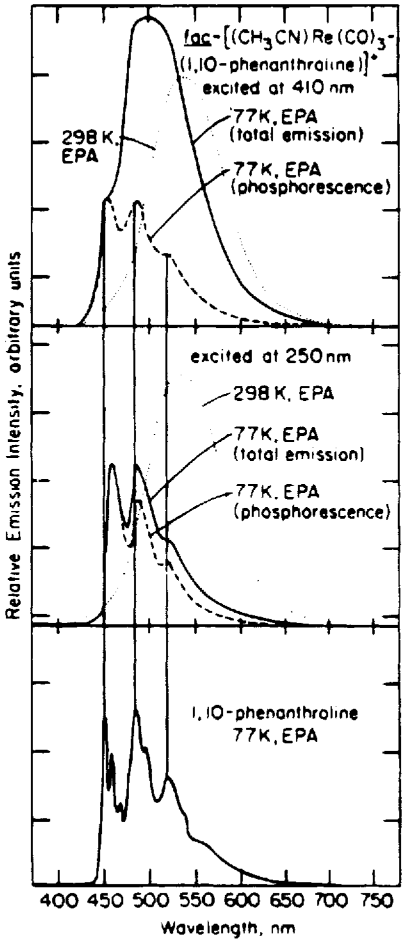


FIGURE 3 Emission spectra excited at 410 nm (top) and 250 nm (middle) for ~ 10^{-4} M *fac*-[(CH$_3$CN)Re(CO)$_3$(phen)](CF$_3$SO$_3$) in EPA. The total emission of phen (bottom) is shown for comparison. The spectra are not shown at the same sensitivity. All spectra are total emission spectra except the two marked "phosphorescence," which were recorded with a phosphoroscope attachment in place. The phosphoroscope allows only the detection of emissions longer than ~50 μs. Data taken from Ref. 14.

$W(CO)_5$ (L = pyz, 4,4-bpy, bpe and bpa) complexes,[15] the multiple-state emitting $CpRe(CO)_2L$ (L = 4-Phpy, 3-BNpy or 4-BNpy) complexes[16] and the *fac*-$XRe(CO)_3L_2$(X = Cl, Br or I, L = 3-BNpy or 4-BNpy) system.[17] In each case, the luminescence bands and the accompanying rigidochromism have been assigned to ^{3}MLCT transitions.

RATIONALE FOR THE LUMINESCENCE RIGIDOCHROMIC EFFECT

As discussed above, it is apparent that the greatest spectral changes that occur between a non-rigid and rigid environment involve MLCT states and, more specifically, triplet-centered ^{3}MLCT levels. Clearly, it is the relatively long-lived electronically excited states which are most perturbed by environmental and associated solvation changes. In contrast, the ^{1}MLCT excited states are relatively unaffected; these levels are anticipated to be extremely short-lived, as they are effectively deactivated by intersystem crossing mechanisms to the ^{3}MLCT excited states and rapid radiationless relaxation processes to the ground state. Indeed, in $W(CO)_5L$ (L = py, pip, 4-CNpy or 4-FMpy) and $Cr(CO)_4(bpy)$, it has been recently shown that the ^{1}MLCT excited states undergo relaxation within a few ps, predominantly via efficient intersystem crossing processes.[18]

Consequently, the luminescence rigidochromic effect can, to a large extent, be related to changes in the solvation environment. Figure 4 portrays a ground-state complex with the surrounding sol-

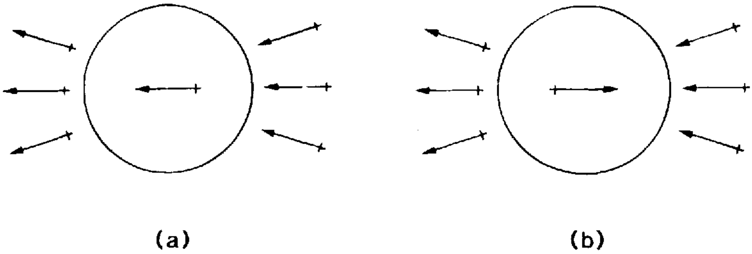


FIGURE 4 Representation of the solvation of (a) a ground-state molecule and (b) a molecule existing in a ^{3}MLCT excited state. Upon excitation the dipole moment of the molecule is depicted to reverse direction.

vent molecules oriented to accommodate the dipole moment. On excitation to the excited state, the complex will possess a different dipole moment and will, thus, be destabilized compared to the ground-state molecule, until the solvent molecules are able to reorient and facilitate a more favorable electrostatic interaction.[19] When the solvent viscosity is substantially increased (which is the case when the solvent passes through the glass transition point on freezing) the ability of the solvent molecules to rearrange the dipole–dipole interactions in the solvent sphere is hindered. Moreover, as a consequence of a reduced free volume in the frozen glass matrix, the solvent molecules can be considered to actually be closer to the excited-state complex, further enhancing the dipolar interactions. It should be noted that the dipole moment of the excited state in Fig. 4 is shown to be reversed, depicting a ^{3}MLCT level where the Re–N bond is contracted relative to the ground state. This representation is in accordance with potential energy descriptions of closely related organometallic complexes.[16b,17b]

It is clear that changes in the solvation of the matrix environment will mainly influence the dipole–dipole forces of the long-lived ^{3}MLCT excited state because it is this level which is normally able to achieve a relaxed form through solvent rearrangement. In an extreme case, where the solvent forms a frozen glass, the motion of the solvent will be so restrained that the solvent dipoles will be unable to effectively reorient themselves about the ^{3}MLCT excited-state molecule. As a consequence, the ^{3}MLCT energy levels will be destabilized in a rigid solvent environment compared to those in a non-rigid one (see Fig. 5). In contrast, these solvation effects will be less influential on the short-lived ^{1}MLCT levels, which will experience much smaller energy perturbations. Using this interpretation makes it possible to explain not only the extent of rigidochromism on the luminescence (^{3}MLCT) and absorption (^{1}MLCT) bands but, also, the direction of the energy shift.

APPLICATIONS OF THE LUMINESCENCE RIGIDOCHROMIC EFFECT

One of the most promising applications of the luminescence rigidochromic effect is to monitor polymerizations in both thermal and photo-

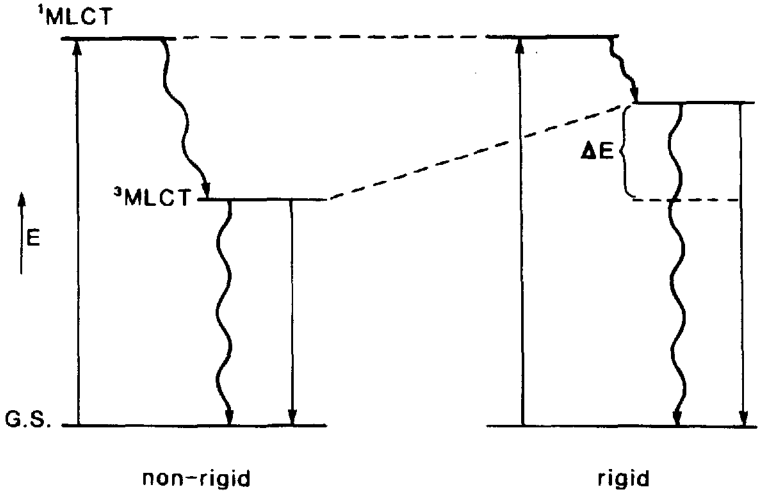
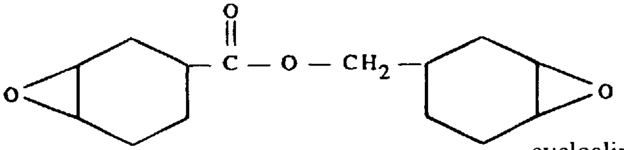


FIGURE 5 Simplified-state energy diagram showing the effect of non-rigid and rigid environments upon the ^{1}MLCT and ^{3}MLCT excited states of rigidochromic organometallic complexes.

chemical polymer systems where the rigidity and, hence, viscosity of the solution will increase dramatically. The luminescence rigidochromic properties of these metal complexes offers a practical way of spectroscopically probing the chemical and physical changes during polymer curing, and this can perhaps be extended to other processes involving materials that undergo environmental changes of a structural nature.

Epoxy resins are a class of thermosetting resins that are widely used in industry because they possess a number of useful properties such as excellent adhesion, corrosion resistance and low cost.[20] They also exhibit a good combination of electrical and mechanical properties and so are used in many electronic applications, such as adhesives, electrical mouldings and matrix resins for protective coatings, dielectrics and encapsulants.[21] Clearly, it is important to be able to monitor the viscosity changes taking place during the thermoset curing.

Recently, significant results involving luminescence rigidochromism have been determined from a study of a cycloaliphatic epoxy (see below) with the *fac*-$XRe(CO)_3L$ (X = Cl, Br or I, L = phen, 4-Me-phen, 4,7-Ph_2Phen or 4,4′-Me_2phen) complex added.[22] In each case, the resins were cured with commercially available amine materials. The organometallic complexes are found to be suitable as luminescent probes because they are soluble and thermally stable throughout the isothermal cure process; these are typically incorporated in small amounts (0.2%, by wt.) in the epoxide. Importantly, they have spectroscopic characteristics (absorption and emission) that are well removed from the resin material.


cycloaliphatic epoxy

Emission spectra observed from *fac*-ClRe$(CO)_3$(4,7-Ph_2-phen) in the cycloaliphatic epoxy resin during three stages of isothermal curing are shown in Fig. 6.[22] Before heating, the resin/probe mixture exhibits dual emission bands at approximately 480 and 600 nm. The higher energy band has been established as being scattered light arising from the resin itself, whereas the lower energy band is a feature of the organometallic complex. On heating, this lower energy band increases intensity significantly, and its energy position blue shifts by ~1,600 cm^{-1}, representing a rigidochromic effect. A plot of the energy position of the probe's ^{3}MLCT emission maximum during the isothermal cure is shown in Fig. 7; this illustrates that substantial environmental changes take place in the middle of the heating process. Table V summarizes the energy shifts that have been observed for all of the *fac*-XRe$(CO)_3$L complexes studied in the cycloaliphatic epoxide system. In each compound a significant rigidochromic effect takes place on the luminescence band.

Photophysical parameters have been obtained from measurements of the emission quantum efficiency and emission lifetime for both the uncured and cured resin materials (see Table VI). Calculated radiative (k_r) and nonradiative (k_{nr}) rate decay constants reveal that in each case k_{nr} decreases by at least an order of magnitude throughout the polymerization. In contrast, k_r is relatively unaltered. Such effects on k_{nr} are consistent with previously measured changes in kinetic

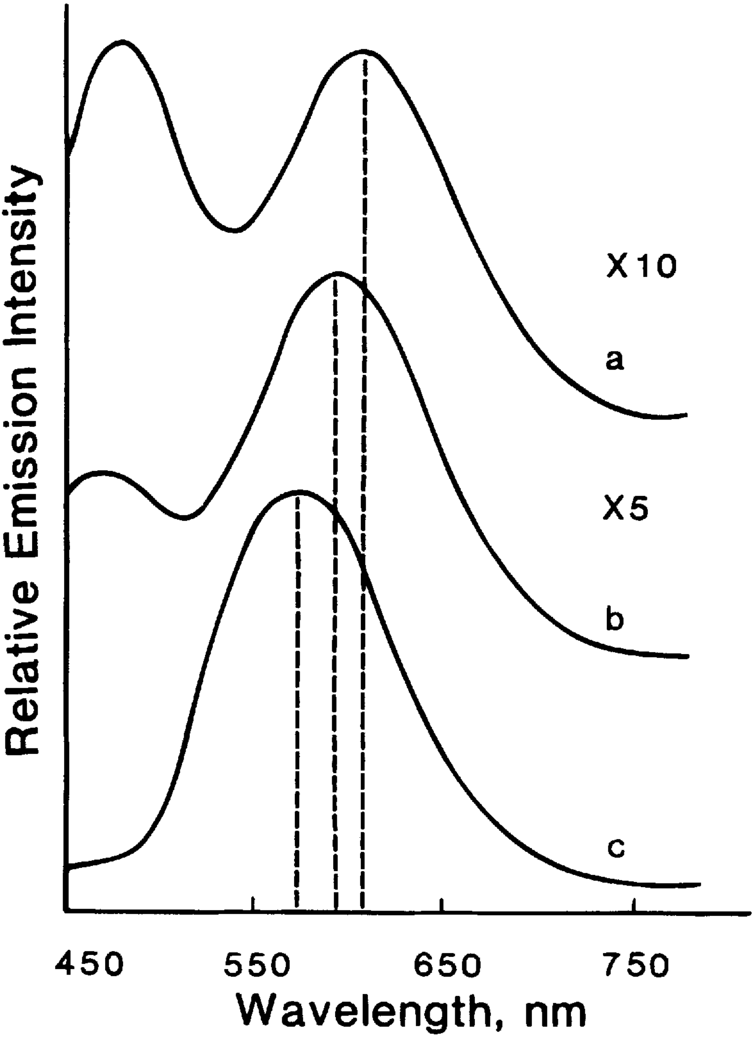


FIGURE 6 Emission spectra of 2 × 10^{-4} M *fac*-ClRe(CO)$_3$(4,7-Ph$_2$-phen) in the cycloaliphatic epoxy/anhydride system at 293 K: (a) before curing; (b) partially cured by heating at 393 K for 30 min; (c) cured by heating at 393 K for 60 min. Excitation wavelength is 400 nm. The emission spectra are uncorrected for wavelength variations in photomultiplier tube response; spectral intensities of (a) and (b) have been scaled ×10 and ×5, respectively. Data taken from Ref. 22.

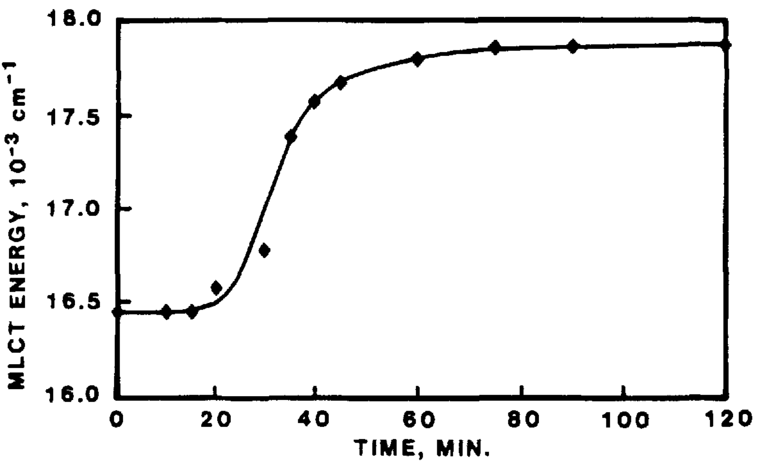


FIGURE 7 Energy position of the uncorrected MLCT emission band maximum of 2×10^{-4} M *fac*-ClRe(CO)$_3$(4,7-Ph$_2$phen) in the cycloaliphatic epoxy/anhydride material as a function of time at the isothermal cure temperature of 393 K. Spectra were acquired at 293 K following excitation at 400 nm. Data taken from Ref. 22.

TABLE V

Absorption (λ_{abs}) and emission (λ_{em}) maxima of the MLCT bands observed from 2×10^{-4} M *fac*-XRe(CO)$_3$L compounds in deoxygenated methylene chloride and the cycloaliphatic epoxy/anhydride system at 293 K[a]

Complex	λ_{abs}, nm CH$_2$Cl$_2$	λ_{em}, nm CH$_2$Cl$_2$	Uncured Epoxy	Cured[b] Epoxy	ΔE_{em}[c], cm^{-1}
fac-ClRe(CO)$_3$(phen)	378	591	592	543	1524
fac-ClRe(CO)$_3$(4-Me-phen)	372	587	575	543	1025
fac-ClRe(CO)$_3$(4,7-Ph$_2$-phen)	381	598	610	556	1592
fac-IRe(CO)$_3$(4,7-Ph$_2$-phen)	410	602	608	581	764
fac-BrRe(CO)$_3$(4,4′-Me$_2$-bpy)	382	587	585	534	1633

[a] Data taken from Ref. 22. Emission spectra are uncorrected for wavelength variations in photomultiplier response; excitation wavelength is 400 nm.

[b] Cured by heating at 393 K for 180 min; observed emission intensity is approximately 10-fold greater than uncured sample.

[c] Energy difference between observed emission bands of the organometallic probes in uncured and cured epoxy samples.

TABLE VI

Photophysical parameters for *fac*-XRe(CO)$_3$L complexes in the uncured and cured cycloaliphatic/anhydride epoxy system at 293 K[a]

Complex	Cure State[b]	ϕ_e[c]	τ_e, ns	k_r, s^{-1}	k_{nr}, s^{-1}
fac-ClRe(CO)$_3$(4,7-Ph$_2$-phen)	uncured	0.042	280	1.5×10^5	3.4×10^6
	cured	0.44	4100	1.1×10^5	1.3×10^5
fac-ClRe(CO)$_3$(4-Me-phen)	uncured	0.039	306	1.3×10^5	3.1×10^6
	cured	0.56	2360	2.4×10^5	1.8×10^5
fac-IRe(CO)$_3$(4,7-Ph$_2$-phen)	uncured	0.048	1049	4.6×10^4	9.1×10^5
	cured	0.56	8100	6.9×10^4	5.4×10^4
fac-BrRe(CO)$_3$(4,4′-Me$_2$-bpy)	uncured	0.035	77	4.5×10^5	1.3×10^7
	cured	0.37	600	6.2×10^5	1.0×10^6

[a] Data taken from Ref. 22. Excitation wavelength is 400 nm.

[b] Cured samples were heated at 393 K for 180 min.

[c] Obtained from corrected emission spectra using emission quantum yield of *fac*-ClRe(CO)$_3$(phen) in deoxygenated CH$_2$Cl$_2$ as a calibrant (Ref. 2).

parameters for radiationless decay pathways of other organometallic[1] and organic molecules[23] upon making the environment rigid in a frozen glassy solution.

It has also been possible to obtain viscosity measurements from the cycloaliphatic resin at various temperatures.[22] Figure 8 illustrates these values and the accompanying changes observed in the energy

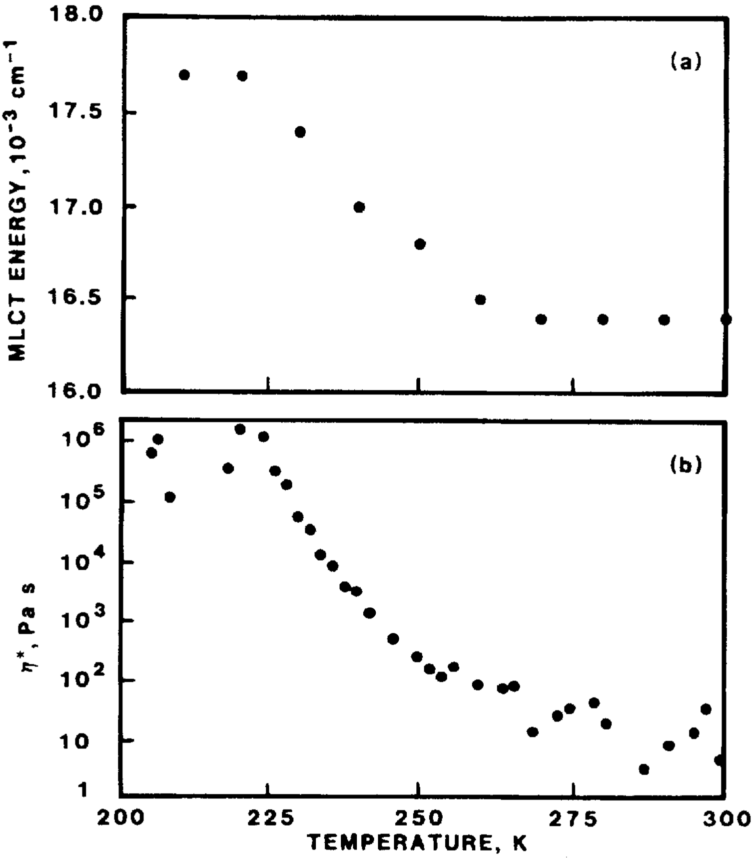


FIGURE 8 (a) Energy position of the uncorrected MLCT emission band maximum of 2×10^{-4} *fac*-ClRe(CO)$_3$(4,7-Ph$_2$-phen) and (b) complex viscosity (η^*) behavior of the neat cycloaliphatic epoxy material as a function of temperature. In (a) the excitation wavelength is 400 nm. Data taken from Ref. 22.

of the ^{3}MLCT emission band over the same temperature range. The blue shift in the emission maximum of the probe complex when the epoxy freezes results in a reversed S-shaped function (Fig. 8a). Complex viscosity (η^*) data acquired from the resin show the same type of dependence (Fig. 8b). Importantly, from these results it has been determined that there is a direct correlation between the viscosity and the observed ^{3}MLCT emission maximum. A semi-log plot depicting this relationship is shown in Fig. 9. It is significant that the shifts in emission of the probe complex are able to parallel the changes in viscosity over such a wide range (5 orders of magnitude in η^*).

Similar observations have been made for an epoxide system involving diglycidyl ether of bisphenol A (DGEBA, see below), a thermosetting system that polymerizes readily at room temperature.[22] Figure 10 depicts changes in the intensity of the probe emission and complex viscosity in DGEBA on addition of (a) amine and (b) polymercaptan curing agents. Clearly, there is once again an excellent correlation between the luminescence and viscosity measurements,

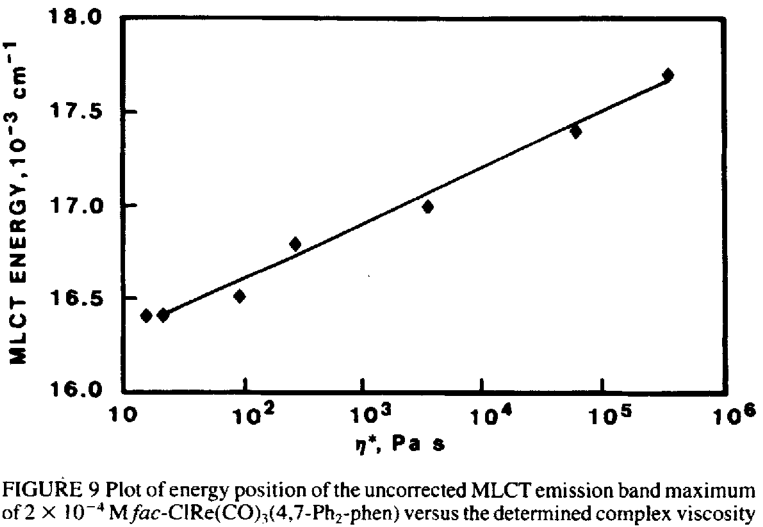


FIGURE 9 Plot of energy position of the uncorrected MLCT emission band maximum of 2×10^{-4} M *fac*-ClRe(CO)$_3$(4,7-Ph$_2$-phen) versus the determined complex viscosity (η^*) values in the neat cycloaliphatic epoxy material. Data taken from Fig. 8 between 220 and 280 K.

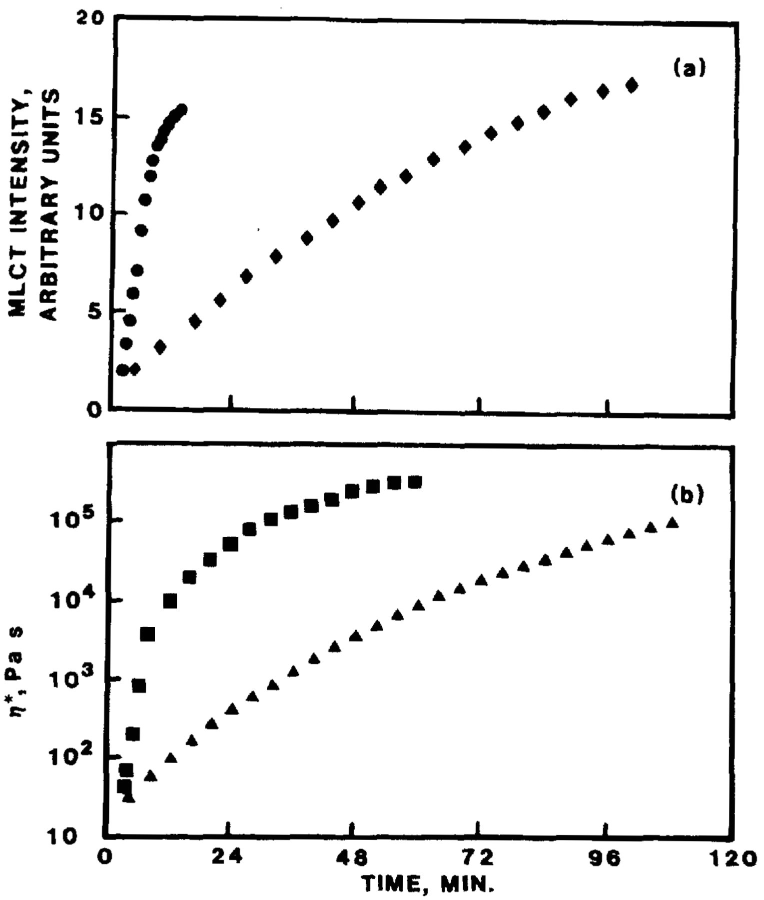
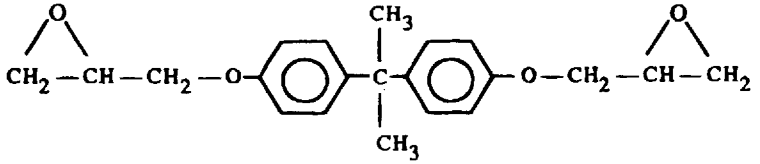


FIGURE 10 (a) Intensity of the MLCT emission at 600 nm of 2×10^{-4} M *fac*-$ClRe(CO)_3(4,7\text{-}Ph_2\text{-phen})$ in the (●) DGEBA/polymercaptan and (◆) DGEBA/amine epoxy materials and (b) complex viscosity (η*) in the (■) DGEBA/polymercaptan and (▲) DGEBA/amine systems as a function of time at the isothermal cure temperature of 293 K. In (a) the excitation wavelength is 400 nm. Data taken from Ref. 22.

illustrating that the *fac*-$ClRe(CO)_3(4,7\text{-}Ph_2phen)$ complex acts as a most sensitive probe for monitoring this polymerization reaction.



diglycidyl ether of bisphenol A

Another major application for these luminescent rigidochromic systems is in thin film polymers that are cured on exposure to light. UV-curable coatings are an important part of the microelectronics industry and are also used in the packaging, graphic arts, medical and dental industries.[24] It is, therefore, highly desirable to develop probe molecules that can monitor the cure kinetics of these processes and yet not interfere with the resin absorption and emission properties or the photoinitiator chemistry. Luminescent organometallic complexes are potentially useful in this regard and offer the attractive feature of often being readily soluble and thermally stable in these non-polar resins.

We have recently investigated the emission of *fac*-$ClRe(CO_3)(4,7\text{-}Ph_2\text{-}phen)$ in an acrylate system involving trimethylolpropane triacrylate (TMPTA) monomer with poly(methyl methacrylate) (PMMA) as a binder.[25] This material undergoes polymerization on light excitation, incorporating 2,2′-dimethoxy-2-phenylacetophenone as a free-radical-producing photoinitiator. Figure 11 illustrates typical emission spectra of *fac*-$ClRe(CO)_3(4,7\text{-}Ph_2\text{-}phen)$ in a photosensitive PMMA:TMPTA (50:50 wt.%) system; the intensity of the ^{3}MLCT emission band is observed to increase approximately three-fold during the course of the excitation. Moreover, there is a small but distinct blue shift in the maximum of this emission band, moving from 576 nm (before irradiation) to 562 nm (after irradiation). Various mixtures of PMMA:TMPTA have been investigated (see Table VII) and in each instance there is a small but reproducible rigidochromic shift as the polymerization proceeds. It is notable that both the magnitude of the rigidochromic effect (ΔE_{em}) and the intensity ratio of the emission (I_f/I_0) is reduced when the PMMA:TMPTA ratio is increased. However, it should be recognized that the viscosity of the

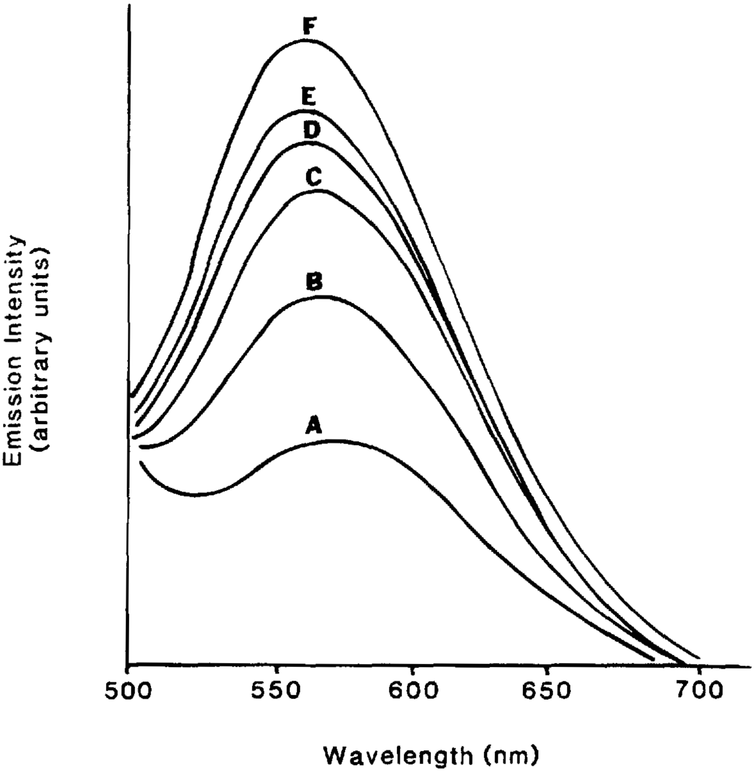


FIGURE 11 Emission spectra of *fac*-ClRe(CO)$_3$(4,7-Ph$_2$-phen) in the model PMMA/TMPTA photosensitive system as a function of UV-irradiation time (s): (A) 0; (B) 5; (C) 10; (D) 20; (E) 30; (F) 60. The emission spectra are uncorrected for photomultiplier tube response and the excitation wavelength is 420 nm. Data taken from Ref. 25.

resin is raised as the PMMA content is increased, so upon light excitation the overall viscosity change during the polymerization will be less.

A closely related photosensitive epoxy resin system involving the DGEBA epoxide with bisphenol A/novalac resin has also been studied.[25b,26] Irradiation of this mixture has been performed via a cation-generating photoinitiator consisting of triarylsulfonium hexafluoro-antimonate salts. Emission spectra recorded from the *fac*-ClRe(CO)$_3$(4,7-Ph$_2$-phen) complex in this photosensitive epoxy sys-

TABLE VII

Emission data of *fac*-ClRe(CO)$_3$(4,7-Ph$_2$-phen) in the photosensitive acrylate system as a function of resin composition[a]

PMMA:TMPTA Ratio (wt%)	λ_{em}, nm[a] Uncured Resin	Cured[b] Resin	ΔE_{em}[c], cm^{-1}	I_f/I_0[d]
30:70	583	561	672	6.9
40:60	580	561	584	4.6
50:50	576	562	432	2.5
60:40	567	562	160	2.1

[a] Data taken from Ref. 25. Emission maxima are uncorrected for photomultiplier response; excitation wavelength is 420 nm.

[b] Following UV-light exposure for 120 s.

[c] Energy difference at the MLCT band maxima between the uncured and cured materials.

[d] Ratio of the initial (I_0) and final (I_f) emission intensities recorded at the MLCT band maxima.

tem at different exposure times are shown in Fig. 12. Dual emission bands are again observed in the spectra. The band at ~460 nm has been attributed to scattered light resulting from the epoxide material itself, whereas the long wavelength feature is due to ^{3}MLCT emission from the organometallic complex. The latter emission band increases substantially and shifts from 581 nm to 522 nm (a blue shift of 1945 cm^{-1}) during the photocure.

Clearly, there are wide-ranging magnitudes of rigidochromic shifts in the above thermosetting and photopolymerization system. The most substantial hypsochromic shifts are observed from the photosensitive (ΔE_{em} = 1945 cm^{-1}) and thermal (ΔE_{em} = 764–1633 cm^{-1}) epoxide matrices. These especially large rigidochromic effects can be related to the highly polar nature [δ = 9.7–10.9 (cal/cm^3)$^{1/2}$] of the cured epoxy network[27] and hence the greater influence of the dipolar interactions and the solvent environment. In comparison, the photosensitive acrylate system gives rise to a lower hypsochromic shift (ΔE_{em} = 160–672 cm^{-1}), and this is perhaps not surprising considering it has a less polar [δ ~ 9.4 (cal/cm^3)$^{1/2}$] network.[27]

Finally, in an entirely different materials application, the emission of *fac*-ClRe(CO)$_3$(bpy) has been used as a probe of the structural changes accompanying the sol-gel processing of silicon and mixed

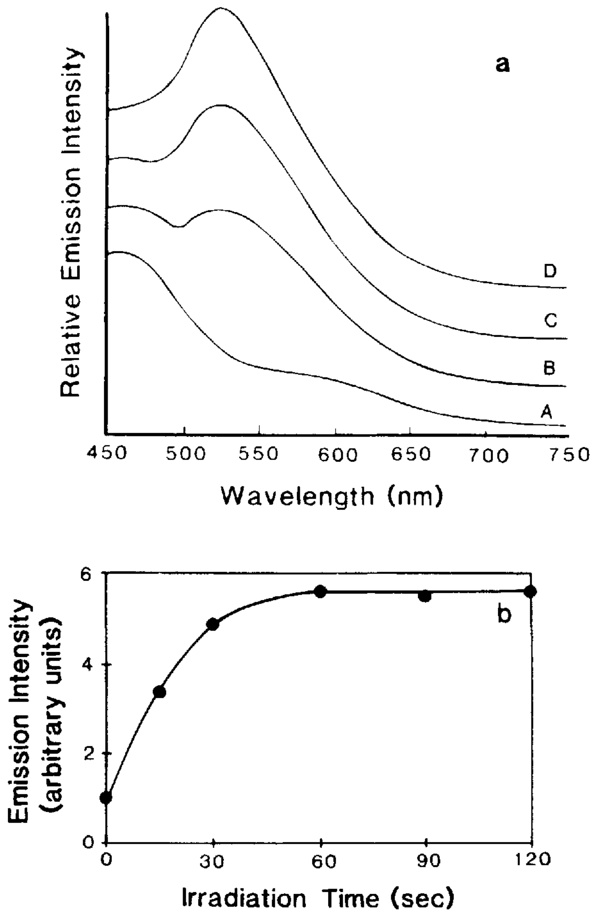


FIGURE 12 (a) Emission spectra of *fac*ClRe(CO)$_3$(4,7-Ph$_2$-phen) in the photosensitive epoxy system at 293 K as a function of UV-irradiation time (s): (A) 0; (B) 15; (C) 30; (D) 60. The emission spectra are uncorrected for photomultiplier tube response and the excitation wavelength is 420 nm. The spectra are vertically displaced for clarity. (b) Plot of emission intensity (recorded at the MLCT band maximum) of *fac*-ClRe(CO)$_3$(4,7-Ph$_2$-phen) as a function of UV-irradiation time. Data taken from Ref. 25.

aluminum–silicon alkoxides.[28] Emission spectra obtained in the aluminosilicate system at various stages of processing are shown in Fig. 13, dramatically illustrating the sensitivity of the probe complex towards rigidity. A plot of the wavelength of the emission band maximum and changes in the weight of the sample in the aluminosilicate sol–gel as a function of time are depicted in Fig. 14. It is clear that the rigidochromic effect provides an excellent way to monitor the structural changes during gelation, aging and drying of silica and aluminosilicate gels in this sol-gel process.

CONCLUDING REMARKS

The luminescence rigidochromic effect demonstrated by several classes of organometallic complexes has recently been characterized

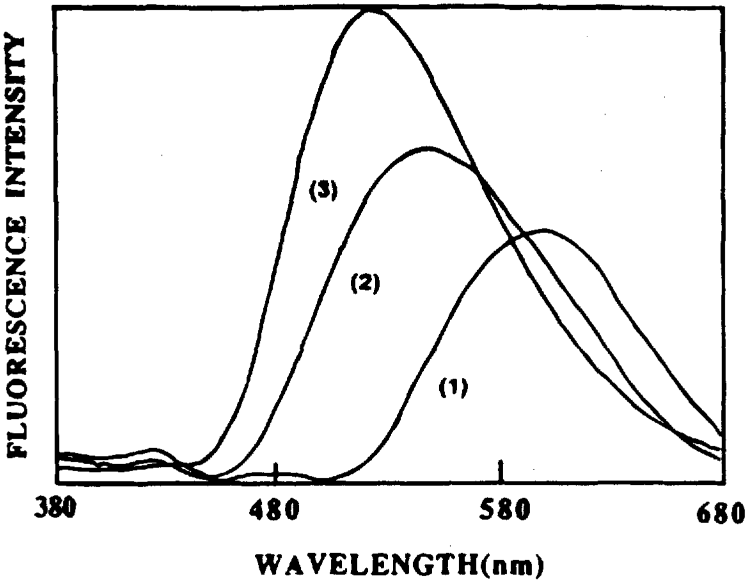


FIGURE 13 Emission spectra of *fac*-ClRe(CO)$_3$(bpy) in the aluminosilicate system at room temperature: (1) initial liquid, (2) aged gel, (3) dried gel. Data taken from Ref. 28.

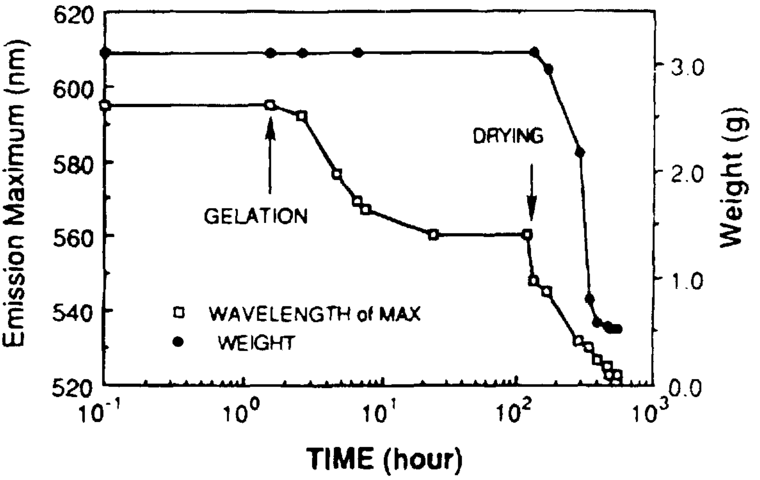


FIGURE 14 Plot of the wavelength of the emission maxima of *fac*-ClRe(CO)$_3$(bpy) in the aluminosilicate system as a function of processing time (lowest curve). The gelation point, the aging period, and the drying period are shown. The concomitant weight changes are shown in the upper curve. Data taken from Ref. 28.

in a wide variety of solvation environments and, consequently, its causes are now becoming much more fully understood. In some cases the emission spectral shifts that are observed are very pronounced and the complexes can be utilized as spectroscopic probes in a number of different material processing applications where viscosity and major environmental changes take place.

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