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Pressure-Induced Luminescence Rigidochromism in the Photophysics of the Cuprous Iodide Cluster $Cu_4I_4py_4$

Dat Tran, James L. Bourassa, and Peter C. Ford*

Department of Chemistry. University of California. Santa Barbara, California 93106

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The effect of applied hydrostatic pressure (up to 275 MPa) on the photophysical properties of the cuprous iodide cluster $Cu_4I_4py_4$ (**I**) in room temperature solutions has been examined. Although there was little pressure effect on emission spectra or lifetimes under conditions where the solutions remained fluid, dramatic hypsochromic shifts in the emission bands occurred when P exceeded that pressure necessary to induce the solvent to undergo the room temperature phase transition from fluid to solid (P_f). For example, in ambient pressure benzene, the $\lambda_{\max}^{\text{em}}$ of the "cluster-centered" (CC) emission of **I** is 695 nm, but at $P \geq P_f$ (72 MPa) this shifts to 575 nm, similar to the $\lambda_{\max}^{\text{em}}$ seen for solid **I** (580 nm). In contrast to the pressure-induced rigidochromism displayed by the luminescence spectrum of **I**, the emission lifetimes proved relatively insensitive to P. Notably, the CC* state of $Cu_4I_4py_4$ represents an unusual example displaying rigidochromism but not solvatochromism in its luminescence. For comparison, analogous pressure studies were also carried on $Re(phen)(CO)_3Br$, a complex which exhibits rigidochromism in luminescence from a metal-to-ligand charge transfer state.

Introduction

The rich photophysical properties of copper(I) and other polynuclear d^{10} complexes have been subject to considerable recent attention.[1,2] One extensively investigated compound is the cuprous iodide cluster $Cu_4I_4py_4$ (**I**, py = pyridine),[1a−d,3−6] which displays a strong, room temperature emission band attributed to a "cluster-centered" excited state (CC*) having mixed iodide-to-metal charge transfer (XMCT) and metal d−s orbital parentage.[3,4,7] The CC* band displays a peculiar sensitivity to the ambiance; its position in fluid solutions is relatively insensitive to solvent identity but is quite responsive to the temperature and rigidity of the medium. For example, $\lambda_{\max}^{\text{em}} = 690$ nm in toluene solution at 294 K but undergoes a strong hypsochromic shift to 583 nm when T is lowered to 77 K.[3] In contrast, solid **I** displays a strong room temperature CC* emission at $\lambda_{\max}^{\text{em}} = 580$ nm which undergoes a bathochromic shift to 619 nm at 77 K.[3] This implies that the blue shift in the solution phase CC* band results from changes in the rigidity of the medium rather than simply from the lowered T. A similar conclusion was drawn by Kunkely and Vogler[5] who noted the $\lambda_{\max}^{\text{em}}$ differences between **I** in fluid benzene solution and in the solid state and also reported that the luminescence spectrum of **I** in polymethylmethacrylate resin displayed a single band (610 nm) closer to that for the solid than for fluid solution. Similar behavior has been termed "luminescence rigidochromism" for other metal complexes with emission spectra dominated by metal-to-ligand charge transfer (MLCT) bands.[8,9] One possible explanation would be that this property reflects significant differences between the ground and excited state structures of **I.** Such a proposal would be consistent with the enormous Stokes shift for the CC* emission[1a] and the surprisingly slow rates of electron transfer from **I*** [6] as well as with *ab initio* calculations[4] which indicate that the Cu_4 core contracts but the Cu−I covalent bonding diminishes in the CC* state. Thus, there is ambiguity regarding whether $Cu_4I_4py_4$ *as a unit* should undergo net expansion or contraction upon excitation.

The present study was initiated with the goal of probing the effect of solvent rigidity on the emission properties of **I** without changing either the temperature or the identity of the solvent. Variation of hydrostatic pressure (P) may be thus used to "tune" solvent properties at a constant temperature.[10,11] Two types of solvents were investigated, those which undergo the transition

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(7) A second band, attributed to emission from an iodide-to-ligand charge transfer (XLCT) state,[3,4] appears at higher energy (480 nm in toluene) but is nearly undetectable at room temperature. This band becomes much more prominent for both solution phase (436 nm in toluene) and solid **I** (438 nm) at 77 K. The appearance of this band at low temperature is a principal source of the "luminescence thermochromism" first described for these materials by Hardt and coworkers.[1b] However, under the conditions of the pressure experiments described here, the weak XLCT band was not observable.

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from fluid to solid phase at a certain applied pressure (P_f) and others which are continuously fluid over the pressure range used. In the former group were benzene ($P_f = 72$ MPa at 298 K),[10] *p*-xylene (36 MPa),[10] and *o*-xylene (229 MPa);[10] in the latter group were toluene and dichloromethane. Presented here are data for the pressure effects in such media over the range 0.1–275 MPa which demonstrate pressure-induced luminescence rigidochromism for **I**. Comparison is made to the photophysical behavior under analogous conditions of the rhenium(I) complex $Re(CO)_3(phen)Br$ (**II**, phen = 1,10-phenanthroline), which has been reported to display luminescence rigidochromism. This property of the Re(I) luminophores has been exploited to probe the rigidity of various solvent media.[9]

Experimental Section

$Cu_4I_4py_4$ was synthesized as described[3] and recrystallized from benzene/hexane. $Re(phen)(CO)_3Br$ was synthesized according to the published method.[12] All solvents were dried over CaH_2 and distilled under nitrogen prior to use.

The procedures for the photophysical measurements under pressure have been described elsewhere.[6,13] Briefly, for a typical experiment, a solution of **I** (~1 mM) was prepared under Ar or N_2 and transferred to the glovebox where a small volume of the stock solution (~0.3 mL) was added to a quartz optical capsule (diameter, ~0.5 cm). A Teflon piston was used to seal the solution inside the capsule. The capsule was placed into a Nova Swiss high-pressure optical cell (model 545.0040) which was filled with H_2O as the pressure-transmitting medium. The high-pressure cell was attached to an Enerpac hand pump via a stainless steel transmitting tubing and gauge, which were used to generate and measure the applied pressure. The temperature of the pressure cell was maintained at 25 °C by a Haake FK circulating water bath.

The apparatus used to record luminescence spectra and lifetimes are similar to that described previously.[13] The excitation source was the third harmonic (355 nm) of a Continuum Model NY-61 Nd:YAG laser (~10 ns pulse width). The emission spectra were monitored at a right angle to the excitation by a spectrograph linked to a CCD detector (Princeton LN/CCD-1024 EUV) which was interfaced to a 486 PC for data manipulation. The emission spectra under pressure were collected by averaging the data from 100 laser shots. Lifetimes were determined by monitoring the emission decay at a single wavelength, usually λ_{max}^{em}, via a monochromator and a RCA 8852 PMT. The PMT output was terminated into a Tektronix TDS 540 digital oscilloscope interfaced to a 486 PC with software for kinetics analysis. All emission spectra were corrected for detector response.

Results

Effects on Emission Spectra and Lifetimes of I. Figure 1 illustrates the luminescence behavior of **I** in benzene solution. At ambient pressure, the CC* emission was seen as a broad band ($\Delta\nu_{1/2}$ = width at half the maximum intensity = 2.6×10^3 cm^{-1}) centered at $\lambda_{max}^{em} = 695$ nm.[14] Increasing the pressure had virtually no effect on the apparent emission intensity, on λ_{max}^{em}, or on $\Delta\nu_{1/2}$ so long as P was less than P_f. For example, at $P = 44$ MPa, the emission band was observed to be centered at 695 nm and appeared to be, within experimental uncertainty, identical to that observed at ambient pressure. Furthermore, there was no effect on the lifetime τ_I derived from the exponential decay of the 695 nm emission. Analogous behavior was the rule for the CC* emission from **I** in other solvents at $P < P_f$, i.e., *pressure effects on* λ_{max}^{em}, were minimal in solvents which remained fluid. This behavior included solutions of **I** in solvents such as toluene and dichloromethane which remained fluid over the entire pressure range investigated (to 275 MPa) (Table 1).

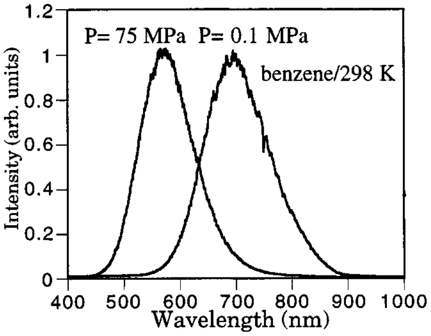

Figure 1. Emission spectra of $Cu_4I_4py_4$ in benzene at ambient pressure and 75 MPa. Both spectra have been normalized to an arbitrary maximum intensity of 1.0.

Table 1. Emission λ_{max}^{em} and Lifetimes of $Cu_4I_4py_4$ and $Re(phen)(CO)_3Br$ in Solution at Different Pressures (P) and in the Solid State

complex	solvent (P_f)[a]	P (MPa)	λ_{max}^{em} (nm)[b]	τ (μs)[c]
$Cu_4I_4py_4$	benzene (72)	0.1	695	8.9
		44	695	8.9
		160	575	9.4
		276	575	9.2
	p-xylene (36)	0.1	700	6.1
		20	700	5.9
		90	572	9.3
		160	572	9.0
	o-xylene (229)	0.1	695	*d*
		276	575	*d*
	toluene (>300)	0.1	700	9.5
		44	700	9.5
		90	700	9.8
		136	700	9.6
	CH_2Cl_2 (1300)	0.1	695	3.2
		206	695	*d*
	solid	0.1	580	11.0
$Re(phen)(CO)_3Br$	benzene	0.1	610	0.50
		175	546	0.17
	solid	0.1	523	0.46

[a] P_f values from ref 10. [b] All emission λ_{max}^{em} values are ±5 nm (see ref 14). [c] All lifetimes are ±10%. [d] Not measured.

In contrast, a sharp discontinuity in the luminescence behavior of **I** was seen when P was raised above P_f. For example, in benzene ($P_f = 72$ MPa), freezing of the bulk solvent was quickly evidenced by the increased scattering of the laser light and emission from the cell as P was raised to 75 MPa. Owing to the much greater light scattering from the frozen solutions, it was impossible to determine quantitatively if the CC* emission was also immediately changed in intensity; however, within 1–2 min, the band at $\lambda_{max}^{em} = 695$ nm disappeared completely with a concomitant growth of the emission band at 575 nm. The change was not instantaneous, nor did the band undergo a gradual shift in λ_{max}^{em}; instead, one band quickly disappeared while the other grew in. This behavior suggests that there are two micro environments experienced by individual $Cu_4I_4py_4$, one favored at $P < P_f$ and the other favored at $P > P_f$, not a continuous array of micro environments from which emission occurs. On the other hand, there was no further measurable effect (given experimental uncertainties) on the apparent emission intensity, on λ_{max}^{em} or on $\Delta\nu_{1/2}$ (~1.8×10^3 cm^{-1}) for frozen solutions as P was again raised from values slightly above P_f to 276 MPa (Table 1).

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(14) Owing to the breadth of these emission bands, a realistic experimental uncertainty in the positions of the maxima is ±5 nm when recorded on the CCD detector.

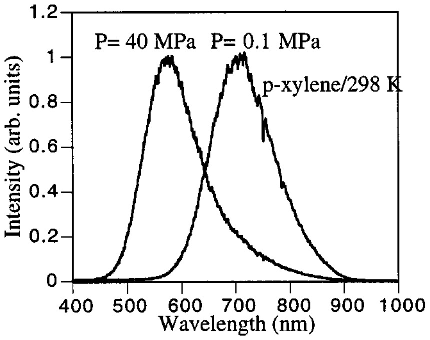

Figure 2. Emission spectra of $Cu_4I_4py_4$ in *p*-xylene solution at ambient pressure and 40 MPa. Both spectra have been normalized to an arbitrary maximum intensity of 1.0.

The observable time delay for the conversion of one emission maximum to another after the bulk solvent appeared to be frozen was a matter of some concern. A simple explanation might be that the microscopic solvation environment of individual molecules of **I** might require some nominal time to freeze, perhaps owing to the slow equilibration of the temperature after release of the heat of fusion. The absence of a gradual shift implies that the molecule is either in a rigid environment or in a fluid one, but not some intermediate stage. Consistent with this explanation is the observation that when P was raised rapidly to a value much higher than P_f the conversion from the 695 nm emission to the 575 nm emission is considerably faster. Also consistent with this explanation was the observation that changes in the emission spectrum of **II** upon pressure-induced solvent freezing showed similar behavior (see below).

The lack of any pressure effects on the CC* emission spectrum so long as solutions of **I** remain fluid indicates that the dramatic shift in λ_{max}^{em} upon freezing must be due to the rigidity of the solvent environment. This conclusion is further examined by taking a frozen solution at $P = 75$ MPa and $T = 298$ K and raising the temperature slowly to 323 K while holding the pressure constant at 75 MPa. Upon melting, the 575 nm emission disappeared and the 695 nm band returned. Lowering T returned the solution to the frozen state, and the band shifted back to 575 nm. The cycle could be repeated with identical results. It is notable that the integrity of **I** was preserved throughout these pressure experiments. The ambient pressure emission spectra, before and after many pressure cycles, were identical in spectral shape as well as intensity in each of the solvents. This observation rules out the possibility of permanent chemical changes induced by changing the pressure.

In contrast to the spectra, the emission lifetimes τ_I of the CC* emission from **I** in benzene proved relatively insensitive to solvent fluidity. Indeed the roughly 5% increase in the lifetimes at 298 K from 8.9 μs in fluid benzene to 9.4 μs observed at pressures above P_f is within generous estimates of experimental uncertainties for lifetime measurements (10%). The room temperature emission lifetime of solid **I** is but 11 μs, so the rigidity of the medium would appear to have little impact upon this parameter. Furthermore, there was virtually no effect of P on τ_I in fluid toluene solutions (9.5−9.8 μs) from increasing P from 0.1 to 136 MPa.

The pressure-induced luminescence rigidochromism of **I**, i.e., shifts in λ_{max}^{em}, was further demonstrated in two other aromatic solvents, *o*-xylene and *p*-xylene. In each case, when the pressure was increased above the P_f (36 and 229 MPa, respectively), solutions of **I** in *o*- and *p*-xylene displayed hypsochromic shifts in λ_{max}^{em} of ~3000 cm^{-1}, but further increasing the applied pressure had little additional effect on λ_{max}^{em} (Figure 2, Table 1). Lifetime measurements did indicate a modest increase of τ_I in *p*-xylene from ~6 μs in fluid *p*-xylene to ~9 μs at $P > P_f$. This may be due to the 50% shorter lifetime of **I*** under ambient conditions in *p*-xylene compared to benzene or toluene, so that there is more room for movement to approach the value for solid **I** in the more rigid medium.

Analogous experiments were also carried out with an air-saturated benzene solution of **I** to probe the effect of pressure on the quenching of CC* by O_2. As expected, the τ_I measured (0.33 μs) from good exponential decay curves at ambient P and T was significantly shorter than that measured under Ar. The concentration of O_2 in an air-saturated benzene[15] can be estimated as 1.8×10^{-3} M, so the change in lifetime would give a second-order quenching constant k_q on the order of ~10^9 M^{-1} s^{-1} in reasonable agreement with earlier studies in this laboratory ($k_q = 6.0\ (\pm 0.6) \times 10^8$ M^{-1} s^{-1} in toluene).[3] Surprisingly, pressure-induced freezing of the benzene solution at $P = 160$ MPa only increased τ_I by a factor of ~2, although, under this condition, the decay of the CC* band clearly did not follow a single exponential. These results imply that a different mechanism for quenching of CC* by O_2 may be involved in the frozen solution since diffusion of O_2 should be dramatically slower. For example, a form of static quenching by O_2 molecules at different distances from the luminactive chromophore might be suggested. Notably, solutions of **I** eventually decomposed when repeatedly excited in the presence of dioxygen.

Pressure Effects on the Luminescence of Re(phen)(CO)$_3$Br. **II** is a representative member of a series of rhenium(I) tricarbonyl complexes with aromatic nitrogen heterocycle ligands which display strong MLCT absorption and emission bands.[8,16] As do other examples of luminactive complexes which have lowest energy MLCT excited states,[9] the emission spectrum of **II** also demonstrates rigidochromic effects and has been exploited as a possible way to probe the microscopic physical properties of curing polymers[9] and sol gels.[17] For example, the λ_{max}^{em} for the MLCT emission band of **II** appears at 610 nm in ambient temperature and pressure benzene solution, but undergoes a substantial hypsochromic shift to 570 nm at 77 K when the solution is a glass. Studies by Salman and Drickamer[18] of Re(phen)(CO)$_3$Cl and similar Re(I) complexes have demonstrated pressure-induced rigidochromism, so **II** is an ideal candidate for testing the pressure system used here to probe the copper clusters.

In this context, the MLCT λ_{max}^{em} of **II** underwent a shift of about 1920 cm^{-1} from 610 nm in ambient pressure benzene solution to 546 nm at 75 MPa, i.e., above P_f at room temperature (Figure 3). Notably, the process was not instantaneous, but instead followed a pattern similar to that seen for **I**; the band centered at 610 nm decreased and that at 546 nm grew in over several minutes. The λ_{max}^{em} was unaffected upon further pressure increase. The position of the band in frozen solution is similar but not identical to the value found for solid **II** (523 nm, Figure 3), consistent with the observations made above for $Cu_4I_4py_4$. However, the lifetime behavior on freezing proved to be somewhat different. Instead of remaining nearly the same or even increasing somewhat, as noted for **I**, τ_{II} measured at λ_{max}^{em} at ambient pressure and at $P \geq P_f$ was 0.50 and 0.17 μs, respectively. The solid gave a lifetime of 0.46 μs at room temperature (Table 1). The hypsochromic shifts in λ_{max}^{em} and

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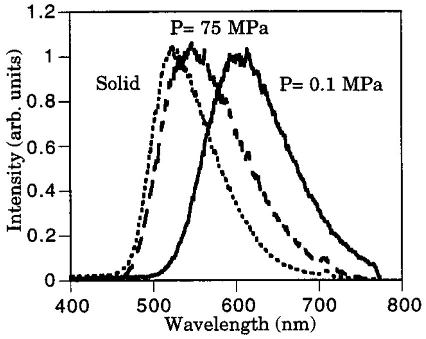

Figure 3. Emission spectra of Re(phen)$(CO)_3$Br in 298 K benzene solution at ambient pressure and at 75 MPa and of solid **II.** The spectra have been normalized to an arbitrary maximum intensity of 1.0.

decrease in τ seen here when a benzene solution of **II** is frozen by pressure were qualitatively similar to the behavior reported previously for the various solutions of the analogous compound $Re(CO)_3$(phen)Cl when subjected to pressures in excess of P_f, although the λ_{max}^{em} shifts for the latter were much smaller.[18]

Discussion

The data described here clearly show that the luminescence rigidochromism demonstrated by the CC* emission of $Cu_4I_4py_4$ when various solutions are frozen by lowering the temperature is indeed a property of the sharply enhanced solution rigidity rather than the result of other perturbations in the system resulting from the temperature change. Pressure alone has but minor effects on the photophysical properties of **I** when the solutions remain fluid. The pressure-induced luminescence rigidochromism of **I** in a solvent such as room temperature benzene, which has a relatively low P_f, is paralleled by the behavior of the rhenium(I) complex $Re(CO)_3$(phen)Br. A recent review, which summarizes luminescence rigidochromism behavior in metal complexes,[9] suggests that this may be limited to complexes such as **II** where the emission bands can be assigned to "triplet" MLCT excited states. Among those systems described, the largest differences between fluid and frozen solution (or other rigid media such as the solid or polymerized solvent) emission maxima are <2000 cm^{-1}. Lees has attributed the luminescence rigidochromism for these ^{3}MLCT emitters to the reduced ability of solvent molecules to reorient in the solid in order to facilitate the most favorable electrostatic interaction with an excited state having a different dipolar character than the respective ground state.[9] Such an explanation is certainly in accord with the solvatochromism often displayed by MLCT absorption[19] and emission[8,20] spectra.

However, for $Cu_4I_4py_4$ and related copper clusters, the behavior of the dominant, lowest energy emission band is clearly not consistent with a ^{3}MLCT assignment for the emitting state.[1a,d,3−5] Both experimental and theoretical results indicate an excited state that has mixed XLCT/d→s character with the acceptor orbital being delocalized over the Cu_4 core. Notably, the emission spectrum from the CC* state is not solvatochromic, yet the luminescence rigidochromic effect is even larger for **I*** (~3000 cm^{-1}) than for ^{3}MLCT emitters such as **II***. Thus, one cannot attribute the pressure-induced luminescence rigidochromism strictly to electrostatic interactions, and some other aspect of the rigidity of the medium must be considered.

Both qualitative considerations and *ab initio* calculations suggest that excitation into the CC* state should enhance metal−metal bonding within the Cu_4 core, but charge transfer from the iodide orbitals should also weaken metal halide bonding. The very large energy differences between the excitation and emission maxima for the CC* luminescence ($\sim 16 \times 10^3$ cm^{-1} in toluene solution)[1a,3] are certainly consistent with major distortions upon excitation. Similarly, earlier work in this laboratory demonstrated that the electron transfer quenching of CC* by various oxidants was surprisingly sluggish and the high over-potentials required for efficient quenching could be interpreted in terms of the large inner-sphere reorganization energy ($\lambda_{in} = 1.4$ eV) required.[6] However, the absence of solvent effects on CC* emission energies suggests that any charge redistribution between the ground and excited state is relatively delocalized. Thus, the hypsochromic effect of freezing the solvent, whether by lowering T or increasing P, may be attributed to an increased energy of the CC* excited state, relative to the ground state, owing to restrictions imposed upon $Cu_4I_4py_4$ expansion by a rigid solvent cavity. In this context, the modest decrease in the width of the CC* emission band ($\Delta\nu_{1/2} = \sim 2600$ cm^{-1} in fluid solution, ~ 1800 cm^{-1} in frozen solvent) suggests a closer correspondence of ground and excited state structures in the more rigid medium.

In summary, the use of hydrostatic pressure offers a convenient method to probe luminescence rigidochromic behavior in solutions without changing other key parameters, especially temperature. This technique has potential applications for photophysical study of other polynuclear transition metal complexes having luminescence properties sensitive to specific solvent environments due to their highly distorted excited states.

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