ELSEVIER

Coordination Chemistry Reviews
208 (2000) 243–266

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

MLCT excited states of cuprous bis-phenanthroline coordination compounds

Donald V. Scaltrito, David W. Thompson,
John A. O'Callaghan, Gerald J. Meyer *

Department of Chemistry, Remsen-Hall, Dunning-Hall, Johns Hopkins University,
3400N Charles Street, Baltimore, MD 21218, USA

Received 27 September 1999; accepted 26 January 2000

Contents

Abstract

Cuprous bis-phenanthroline compounds possess metal-to-ligand charge transfer, MLCT, excited states. Phenanthroline ligands coordinated to Cu(I) that are disubstituted in the 2- and 9-positions with alkyl or aryl groups, abbreviated $Cu^I(phen')_2^+$, have long-lived excited states at room temperature. The parent $Cu^I(phen)_2^+$ compound is non-emissive under the

---

* Corresponding author. Tel.: + 1-410-5167319; fax: + 1-410-5168420.
E-mail address: meyer@jhuvms.hcf.jhu.edu (G.J. Meyer).

PII: S0010-8545(00)00309-X

same conditions with a short excited state lifetime, $\tau < 10$ ns. Disubstitution in the 2,9-positions stabilizes the Cu(I) state and increases the energy gap between the MLCT and the ground state. The prototypical and most well studied compound is $\mathrm{Cu^I(dmp)_2^+}$, where dmp is 2,9-$\mathrm{(CH_3)_2}$-1,10-phenanthroline. In dichloromethane solution at room temperature, $\mathrm{Cu^I(dmp)_2^+}$ displays broad MLCT absorption with $\lambda_{\mathrm{max}} = 454$ nm, a broad unstructured emission with $\lambda_{\mathrm{max}} = 730$ nm, and an excited state lifetime of 85 ns. The emission arises from two closely spaced MLCT excited states, separated in energy by 1800 $\mathrm{cm^{-1}}$, that behave as one state at room temperature. $\mathrm{Cu^I(dmp)_2^{+*}}$ excited states are quenched in the presence of Lewis bases and coordinating solvents. A 5-coordinate excited state complex, or exciplex, is proposed to account for temperature dependent quenching data. The substantial inner-sphere reorganizational energy changes that follow light excitation are novel features of these MLCT excited states. This review attempts to cover all the existing data reported on $\mathrm{Cu^I(phen')_2^+}$ excited states and contrast it with well-known MLCT behavior of $(\mathrm{d}\pi)^6$ transition metal compounds.

Keywords: Copper; MLCT excited states; Exciplex; Photophysics

1. Introduction

Coordination compounds can be aesthetically pleasing due to the wide range of colors that are exhibited [1–3]. These colors arise from electronic transitions of various types. One particular type of electronic transition that will be intimately related with this review is the metal-to-ligand charge transfer (MLCT). For transition metal compounds, the promotion of an electron from a metal d orbital to a low lying anti-bonding π^* level of an organic ligand is often observed. This transition can be represented by Eq. (1). Research over the last 20 years has focused on developing a molecular-level understanding of MLCT excited states, particularly those derived from $(\mathrm{d}\pi)^6$ transition metal

$$[\mathrm{d}\pi]^n[\pi^*]^0 \rightarrow [\mathrm{d}\pi]^{n-1}[\pi^*]^1 \tag{1}$$

compounds, in fluid solution [4–8]. The desirable properties of MLCT excited states have been exploited recently for practical applications in areas such as solar energy conversion [9], chemical sensing [10], photo-catalysis [11], and displays, as well as in molecular probes for biology [12] and materials science [13].

There is an extensive excited state and redox chemistry based on second and third row transition metals utilizing bi- or tri-dentate aromatic heterocyclic ligands [4–8]. The classic example is, of course, $\mathrm{Ru^{II}(bpy)_3^{2+}}$ where bpy is 2,2′-bipyridine. This is probably the most well studied coordination compound in history, with over 7000 research papers being published on it. This compound has highly desirable properties including microsecond lifetimes in fluid solution, intense visible absorption and emission, well defined redox chemistry, and high stability under many conditions [4–8]. Practical devices based on Ru(II) polypyridyl derivatives now exist for $\mathrm{O_2}$ sensing [14] and solar energy conversion [15]. However, there are some potential drawbacks of Ru(II)-based devices, including high costs and environmental concerns. Existing alternatives, such as Re(I) and Os(II), have these same inherent limitations [4–8]. It is therefore worthwhile to develop alternatives that circumvent these difficulties.

An attractive alternative is emerging in the form of (dπ) 10 transition metal compounds, particularly Cu(I) coordination compounds [16,17]. In fact, Cu(I) diimines are the only first row-transition metal compounds with excited state properties that are at all comparable to $Ru^{II}(bpy)_3^{2+}$. Cuprous diimine complexes generally absorb UV–vis light over the range of 350–650 nm with relatively high extinction coefficients ($\varepsilon \sim 10^3$–10^4 M^{-1} cm^{-1}). With phenanthroline ligands that possess alkyl or aryl substituents in the 2- and 9-positions, the MLCT excited states are emissive with 10^{-9}–10^{-7} s lifetimes at room temperature (r.t.) in CH_2Cl_2 solution [16,17]. Copper is less toxic, expensive, and environmentally hazardous than ruthenium.

Here, we present a review of cuprous bis-phenanthroline MLCT excited states and an analysis of the available data. The phenanthroline ligands used throughout the review are given in Fig. 1. In some cases, the notation $Cu^{I}(phen')_2^{+}$ is given where phen′ could be any of the phenanthroline derivatives shown in Fig. 1. The review is organized as follows. We begin with a short discussion of the redox and structural properties of copper phenanthroline compounds that serve as background. The published copper MLCT excited state literature is then presented followed by an analysis based on accepted models. We conclude with some directions for future research.

2. Background

2.1. Structural properties

An interesting property inherent to copper coordination compounds is the structural difference between the Cu(I) and Cu(II) oxidation states [18]. Cu(I) is d^{10} and generally prefers to be four-coordinate with a nearly tetrahedral geometry. Cu(II) is d^9 and adopts a Jahn–Teller distorted geometry that is usually 5- or 6-coordinate [18]. This inner sphere reorganizational change is novel to Cu(II/I) redox chemistry and has important consequences in the MLCT excited state behavior.

A review of Cu(I) bis-phenanthroline and bis-bipyridine crystal structures show considerable deviation from the tetrahedral geometry [19–23]. Typically, the angle between the two diimine ligands is less than the idealized 90°. This flattening of the ligands (towards a square planar geometry) lowers the symmetry from D_{2d} to D_2. Since the solid state structure is influenced by crystal packing forces, it might be expected that the solution geometry of $Cu^{I}(phen')_2^{+}$ is closer to tetrahedral. While no detailed studies of the solution structure have been performed, to our knowledge, the ^{1}H-NMR reported in CH_2Cl_2 or CH_3CN are sharp, with equivalent phenanthroline and substituent resonances on the NMR time scale at r.t. [24]. The symmetry in fluid solution is unknown however, and has frustrated attempts to develop a group theoretical description of the Franck–Condon excited states.

In fluid solution, Cu(I) bis-phenanthroline compounds are known to be labile. For example, immediately after mixing Cu^{I}(dmp)$_2^+$ and Cu^{I}(bcp)$_2^+$ a ^{1}H-NMR spectra revealed the presence of the mixed chelate, Cu^{I}(dmp)(bcp)$^+$ [27]. The replacement of 2,2′-biquinoline ligands coordinated to Cu(I) by dmp also occurs in fluid solution [28]. A novel approach has been described recently to inhibit ligand scrambling [29]. By utilizing a phenanthroline ligand with tertiary butyl groups in the 2- and 9-positions of phenanthroline (dtbp), the formation of Cu^{I}(dtbp)$_2^+$ is inhibited by the steric bulk of the *t*-butyl subsituents. The mixed chelate compound was then easily prepared and isolated, Cu^{I}(dtbp)(dmp)$^+$. The compound was stable in dichloromethane, but ligand exchange to form Cu^{I}(dmp)$_2^+$ and Cu^{I}(dtbp)S$_2^+$ (where S = solvent) in acetonitrile and dimethylsulfoxide was reported [29]. While the mechanism for these processes and other experimental details are currently lacking, it is clear that Cu(I) is labile and that ligand exchange in fluid solution can

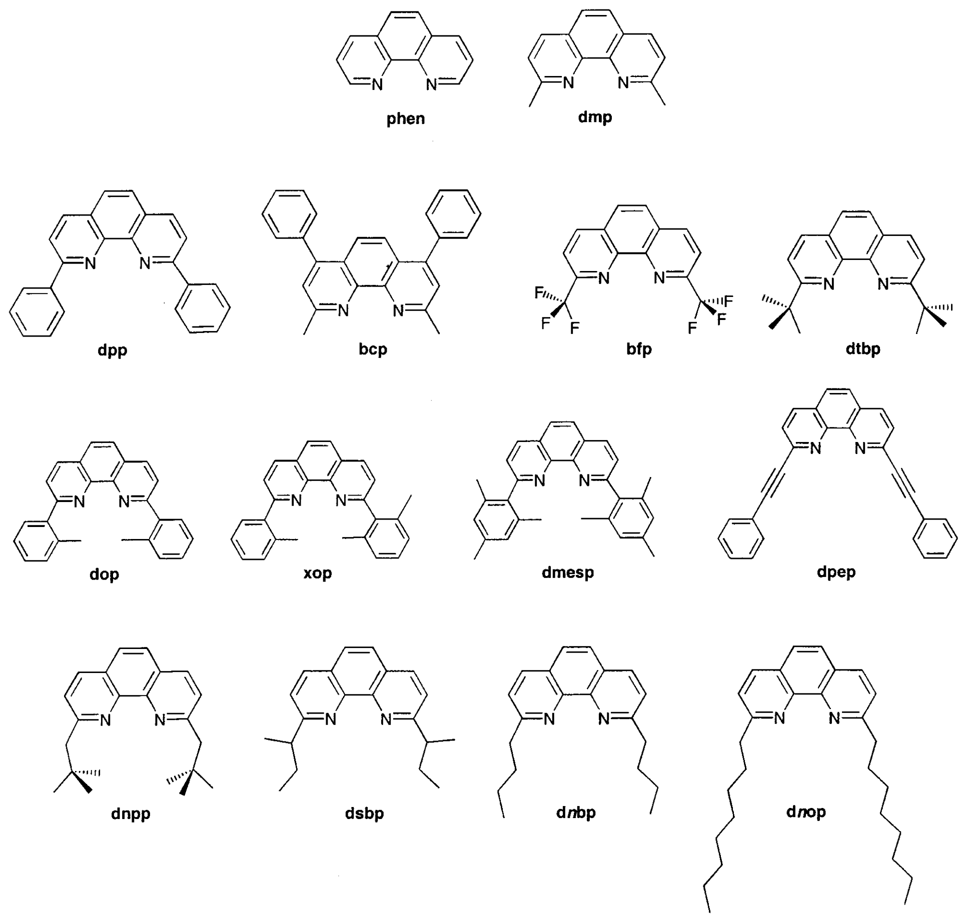


Fig. 1. The 1,10-phenanthroline ligands and their abbreviations used throughout the text.

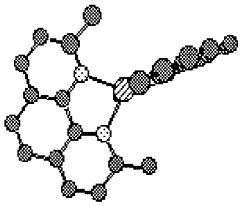
be facile. This may be an impediment to some applications of Cu(I) bis-phenanthroline excited states.

Crystal structures of Cu(II) bis-phenanthroline or bis-bipyridine compounds are numerous. A large class of compounds of the general form $Cu^{II}(phen')_2X^+$ and $Cu^{II}(bpy')_2X^+$ are known, where X is a halide, pseudohalide, or counterion [30–38]. Examples where the fifth ligand is derived from solvent are also known, for example $Cu^{II}(dmp)_2(H_2O)^{2+}$ [38]. While the vast majority of Cu(II) compounds possess geometries that lie between the trigonal bipyramidal and square pyramidal extremes, there do exist a few examples of six-coordinate Cu(II) bis-bipyridine compounds [40–42]. The term plasticity has been introduced to describe the non-rigid, eccentric nature of Cu(II) ions [39].

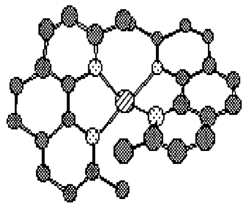
Some effort has been set forth to prepare four coordinate Cu(II) phenanthroline or bipyridine compounds [25,43]. This has been accomplished by two different approaches. The first is to crystallize the compounds in weakly coordinating solvents with weakly coordinating anions. In fact, $Cu^{II}(bpy)_2^{2+}$ has been crystallized from dichloromethane as a PF_6^- salt [43,44]. An alternative strategy has been to employ phenanthroline ligands with substituents in the 2- and 9-positions that inhibit higher coordination numbers [44]. An example of this is 2,9-diphenyl phenanthroline, dpp, where X-ray crystallography reveals that both $Cu^{I}(dpp)_2^{2+}$ and $Cu^{II}(dpp)_2^{2+}$ are four-coordinate [25]. Here the phenyl substituents prevent the two phenanthroline ligands from attaining a square planar geometry and inhibit access of incoming Lewis bases to the metal center.

2.2. Electrochemical properties

Over 35 years ago, James and Williams proposed that substituents in the 2- and 9-positions of 1,10-phenanthroline, when coordinated to Cu(I), would interact in a destabilizing manner with the 2- and 9-substituents on the opposite ligand in the cupric state [44]. They argued that this interaction would dramatically stabilize the cuprous state. Electrochemically, they found that it was over 400 mV easier to oxidize $Cu^{I}(phen)_2^+$ than $Cu^{I}(dmp)_2^+$ in aqueous electrolyte. We observed a similar shift in less coordinating 0.1 M tetrabutylammonium hexafluorophosphate–CH_2Cl_2 solution [24]. This observation can not be rationalized through inductive effects of the methyl groups or coordination number changes. Rather, it is most easily rationalized through steric effects, as the two dmp ligands can not achieve a high degree of planarity with respect to one another in the cupric state, as is shown schematically.



$Cu^{I}(dmp)_2^+$



$Cu^{II}(dmp)_2^{2+}$

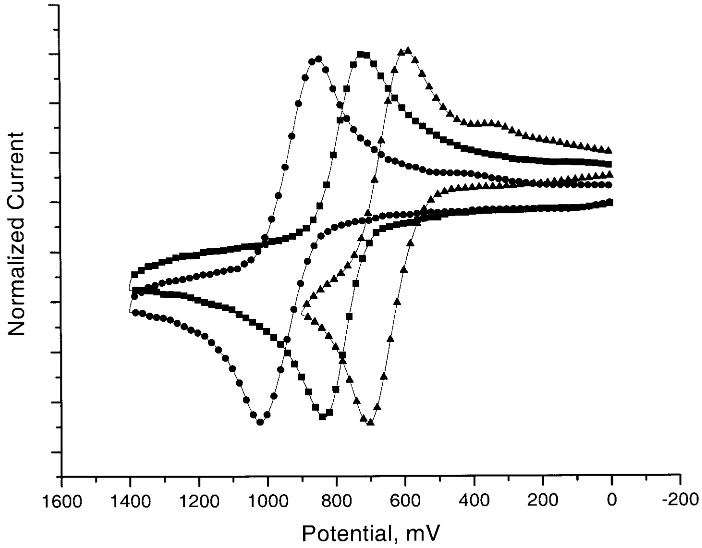


Fig. 2. Cyclic voltammograms of $Cu^I(dmp)_2^+$ in CH_2Cl_2 (circles), CH_3CN (squares), and DMSO (triangles) measured at 200 mV s^{-1} with a common electrolyte, 0.1 M tetrabutylammonium hexafluorophosphate, a Ag wire reference electrode, a Pt gauze auxillary electrode, and a glassy carbon working electrode. The potentials measured versus SCE are given in the text.

A less well appreciated aspect of Cu(II/I) redox chemistry is the solvent dependence. In examining the voltammetry of $Cu^I(dmp)_2(PF_6)$, we found that the measured half-wave potential, $E_{1/2}$, assigned to the Cu(II/I) couple was surprisingly sensitive to solvent [45]. For example, $E_{1/2}$ is 0.93 V in CH_2Cl_2, 0.77 V in CH_3CN, and 0.64 V in DMSO with a common electrolyte versus a Ag wire reference shown in Fig. 2. Assuming that the diffusion constants of the oxidized and reduced complexes are the same, $E_{1/2}$ is equivalent to the formal reduction potential, $E°$ [46]. The peak-to-peak separation measured were typically 100–200 mV and essentially independent of solvent. The anodic and cathodic peak currents were equivalent within experimental error, $i_{pa}/i_{pc} \sim 1$, and plots of the square root of peak current versus the scan rate were linear from 10 to 200 mV s^{-1}, as expected for a diffusional process. A ferrocene standard showed only a slight dependency of $E_{1/2}$ with solvent.

The simplified scheme used to model this data is shown below. Oxidation of Cu(I) to Cu(II) at the electrode surface is followed by addition of solvent to the oxidized complex. We assume that solvent coordination is fast and reversible with respect to the cyclic voltammogram time scale and that concentration of the five-coordinate Cu(I) compound, $Cu^I(dmp)_2(S)^+$ is negligibly small. The fact that $i_{pa}/i_{pc} \sim 1$ and that only a single wave is observed are consistent with these assumptions. Therefore, establishment of the solvent binding equilibrium, $K_s = k_f/k_r$, lowers the free energy for electron transfer by $RT \ln K_s$. Using simple thermodynamic cycles, and assuming that adduct formation does not occur in weakly coordinating CH_2Cl_2, an equilibrium constant K_s of 10^5 M^{-1} is estimated in DMSO and 10^3 M^{-1} in CH_3CN [46].

$$\mathrm{Cu^{I}(dmp)_2{}^{+}} \underset{+\,e\text{-}}{\overset{-\,e\text{-}}{\rightleftharpoons}} \left[\mathrm{Cu^{II}(dmp)_2{}^{2+}} + \mathrm{S} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{Cu^{II}(dmp)_2(S)^{2+}}\right]$$

The shift of $E_{1/2}$ with solvent is not manifest in the visible absorption spectrum of $Cu^I(dmp)_2^+$. The visible absorption spectra are, within experimental error, the same in all solvents examined with only small changes in the extinction coefficients. This is expected since light absorption is a vertical process in the Franck–Condon sense and, unlike cyclic voltammetry, is not influenced by processes that occur after charge transfer. A consequence of this is that the expected correlations between optical energy gaps and metal based reduction potentials that exist for $(d\pi)^6$ transition metal compounds are not observed [4–8]. This point will be expanded upon toward the end of the following section.

3. Copper MLCT excited states

3.1. Non-emissive compounds

Cu(I) bis-phenanthroline compounds have been known for quite some time. The red color in solution was first postulated to arise from an MLCT transition by Irving and Williams in the early 1950s [47]. However, direct experimental evidence for this postulation eluded researchers. Also lacking were any observations of photoluminescence from MCLT excitation.

3.2. $Cu^I(dmp)_2^+$

Until 1980, photoluminescence (PL) from cuprous diimine excited states had been confined to low temperature rigid media or the solid state [48]. An important advance was made by McMillin and coworkers when they reported the first observation of ambient temperature PL from $Cu^I(dmp)_2^+$ in CH_2Cl_2 solution [49]. The corrected PL spectra, which showed a dramatic red shift relative to the ground state absorption maximum, is broad and structureless with a PLI_{max} at 730 nm, Fig. 3, making detection difficult both by the sensitivity of the naked eye and photomultiplier tubes. The excited state lifetime is 85 ns and the emission quantum yield is 2×10^{-4}.

The excited states of $Cu^I(dmp)_2^+$ are well formulated as MLCT. Therefore, light absorption promotes an electron from the d orbitals of copper to the π^* orbitals of the ligand. The excited state is formally a Cu(II) metal center coordinated to a reduced ligand, $[Cu^{II}(dmp)(dmp^-)]^{+*}$. Nanosecond transient absorption spectroscopy of $Cu^I(dmp)_2^+$, along with other bidentate aromatic nitrogen ligands coordinated to Cu(I), supports this assignment [24]. Additionally, time resolved

Raman spectroscopy reveals that the excited electron is localized on one ligand [50,51].

Eqs. (2)–(5) represent fundamental relationships between physically measurable parameters and underlying photophysical properties of excited states [52]. The excited state lifetime, τ, is related to the radiative rate constant, k_r, and the non-radiative rate constant, $k_{nr,}$ through Eq. (2). The emission

$$\tau = (k_r + k_{nr})^{-1} \tag{2}$$

$$\phi_{em} = \eta^* k_r (k_r + k_{nr})^{-1} \tag{3}$$

quantum yield, ϕ_{em}, is related to these same parameters through Eq. (3), where η is the quantum yield for intersystem crossing from upper excited states to the emissive excited state, usually assumed to be 1. Therefore by measuring the excited state lifetime and emission quantum yield, k_r and k_{nr} can be calculated directly by Eqs. (4) and (5) assuming that $\eta = 1$.

$$k_r = \phi_{em}/\tau \tag{4}$$

$$k_{nr} = (1 - \phi_{em})/\tau \tag{5}$$

Applying these equations to $Cu^I(dmp)_2^+$ in CH_2Cl_2, k_r and k_{nr} are calculated to be 2.7×10^3 and 1.8×10^7 s^{-1}, respectively (Table 1). We note that the quantum yields for emission are probably underestimated due to poor PMT sensitivity at long wavelengths. Therefore, a systematic bias is inherent in these values and a cautious interpretation is required.

It was postulated that only Cu(I) coordination compounds with fairly bulky substituents, i.e. $-CH_3$ or $-C_6H_5$, in the 2- and 9-positions of phen would be emissive in poorly coordinating solvents [49]. Other disubstituted phenanthroline compounds of Cu(I) are in fact emissive while $Cu^I(phen)_2^+$ is not, Fig. 3. Room temperature PL from $Cu^I(dmp)_2^{+*}$ is not observed in solvents such as water,

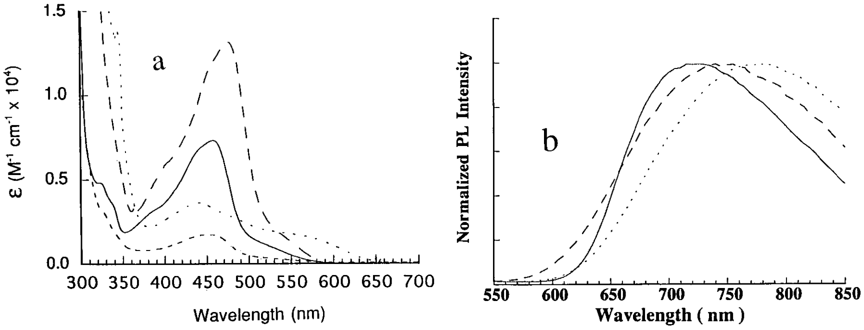


Fig. 3. Panel (a) displays room temperature visible absorption spectra of (- - - - -) $Cu(phen)_2(PF_6)$; (---- ---- ----) $Cu(bcp)_2(PF_6)$; (——) $Cu(dmp)_2(PF_6)$; and (-- -- -- --) $Cu(dpp)_2(PF_6)$ in dichloromethane. Panel (b) shows the corrected photoluminescence spectra of (-- -- -- --) $Cu(bcp)_2(PF_6)$; (---- ---- ----) $Cu(dmp)_2(PF_6)$; and (——) $Cu(dpp)_2(PF_6)$ in dichloromethane. The samples were excited with 460 ± 2 nm light.

ethanol, acetonitrile, and acetone [49]. Detailed thermodynamic analysis of PL quenching of $Cu^I(dmp)_2^{+}{}^*$ in dichloromethane, as a function of temperature and added Lewis bases, reveals that a reversible complex is formed between the Lewis base and excited state before the excited state is quenched [53–55]. It was concluded that some solvents can act as a Lewis base and stabilize the formally Cu(II) metal center in the excited state. A five coordinate excited state complex, termed exciplex, was postulated. Exciplex formation was proposed to stabilize the excited state and increase the non-radiative decay rate constant, thereby shortening the lifetime of the excited state [53–55]. In agreement with this proposal, the excited state lifetime of $Cu^I(dmp)_2^{+}{}^*$ was found to be 2 ns in CH_3CN solution [56]. Furthermore, volumes of activation determined for $Cu^I(dmp)_2^{+}{}^*$ quenching are consistent with a higher coordination number expected for an excited state adduct [57].

The excited state reduction potentials can be estimated from ground state reduction potentials and the corrected emission spectra, as given by Eq. (6),

$$E_{1/2}(\mathrm{Cu}^{\mathrm{II/I}*}) = E_{1/2}(\mathrm{Cu}^{\mathrm{II/I}}) - \Delta G_{\mathrm{es}} \tag{6}$$

where $E_{1/2}(\mathrm{Cu}^{\mathrm{II/I}})$ is the ground state reduction potential and ΔG_{es} is the free energy stored in the thermally equilibrated excited state. Similarly, the excited state oxidation potential can be estimated using Eq. (7),

$$E_{1/2}(\mathrm{Cu}^{\mathrm{I}*/0}) = E_{1/2}(\mathrm{L}^{0/-}) - \Delta G_{\mathrm{es}} \tag{7}$$

where $E_{1/2}(\mathrm{L}^{0/-})$ represents a phen ligand reduction potential. Hence, $Cu^I(dmp)_2^{+}{}^*$ is a potent photoreductant, with an $E_{1/2}(\mathrm{Cu}^{\mathrm{II/I}*}) \approx -1.4$ V versus SCE [17]. The compound is only a mild photooxidant, $E_{1/2}(\mathrm{Cu}^{\mathrm{I}*/0}) \approx -0.1$ V versus SCE [27].

In the mid 1980s, McMillin et al. reported spectroscopic evidence for the participation of two excited states near r.t. [58]. At -30°C, the excited state of $Cu^I(dmp)_2^+$ displays nonexponential decay kinetics that were fit to a biexponetial model. At ambient temperature, the fast component in the PL spectra vanishes, leaving only a single exponential kinetic decay. The temperature dependence of the PLI suggests involvement of at least two excited states. A model was proposed with two low lying MLCT excited states are separated in energy by $\approx 1800\ \mathrm{cm}^{-1}$ [58]. They calculated radiative rate constants to be on the order of $10^3\ \mathrm{s}^{-1}$ for the lower excited state and $10^7\ \mathrm{s}^{-1}$ for the upper excited state [58].

The vibrational characteristics of $Cu^I(dmp)_2^+$ and it's MLCT excited state have been probed by McGarvey et al., using both resonance Raman and time resolved resonance Raman (TR^3) spectroscopy [50,51]. The motivation for these studies was to determine whether the excited electron was delocalized over both dmp ligands, $[(dmp^{-1/2})Cu^{II}(dmp^{-1/2})]^{+*}$, or only localized over one dmp ligand, $[(dmp)Cu^{II}(dmp^{-1})]^{+*}$. The results are shown in Fig. 4 for $Cu^I(dmp)_2^+$ probed in both MeOH and CH_2Cl_2 [14a]. In MeOH, the excited state is readily quenched and the excited state lifetime is shorter than the laser pulse, $\tau < 8$ ns. Thus, the spectrum is assigned to scattering from the ground state, i.e. neutral ligand modes. In CH_2Cl_2, the excited state is long lived and can be probed spectroscopically, with a $\tau = 85$ ns. Analysis of the spectrum shows only scattering from neutral ligand modes, specifically at $1320\ \mathrm{cm}^{-1}$. Control experiments using the heteroleptic

Table 1
Photophysical properties of Cu(I) phenanthroline compounds in CH_2Cl_2 at room temperature

Compound[a]	Abs (nm)[b]	PLI_{max} (nm)[c]	$E_{\text{abs}}-E_{\text{em}}$ (eV)[d]	$\phi_{\text{em}}\times 10^{3}$[e]	τ (ns)	k_r ($\times 10^3$ s^{-1})[f]	k_{nr} ($\times 10^7$ s^{-1})[f]
$Cu^{I}(phen)_2^+$	458						
$Cu^{I}(dmp)_2^+$	454	730	1.05	0.23	85	2.71	1.18
$Cu^{I}(dpp)_2^+$	448	715	1.04	2.50	280	8.93	3.56
$Cu^{I}(bcp)_2^+$	478	765	0.97	0.25	80	3.13	1.25
$Cu^{I}(bfp)_2^+$	462	665	0.81	3.30	165	24.00	0.60
$Cu^{I}(dnpp)_2^+$	449	715	1.03	1.60	260	6.15	0.38
$Cu^{I}(tptap)_2^+$	490	715	0.81	1.00	150	6.67	0.67
$Cu^{I}(dipp)_2^+$	445	680	0.96	4.00	365	10.90	0.27
$Cu^{I}(d\textit{s}bp)_2^+$	455	690	0.92	4.50	400	11.25	0.25
$Cu^{I}(dtbp)(dmp)^+$	440	646	0.90	10.00	730	13.70	0.14

[a] Copper coordination compounds where the ligand abbreviations are shown in Fig. 1. All compounds have a PF_6^- counterion.
[b] Absorption maximum ± 4 nm.
[c] Corrected photoluminescence maximum.
[d] Energy separation between the absorption and emission maxima.
[e] Quantum yields for photoluminescence.
[f] Radiative, k_r, and non-radiative, k_{nr}, rate constants calculated using Eqs. (4) and (5).

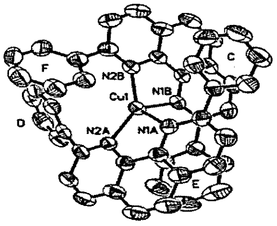
$Cu^{I}(dmp)(PPh_3)_2^+$ (PPh_3 = triphenylphosphine) in MeOH, when excited at 355 nm, shows no scattering from neutral ligand modes near 1320 cm^{-1}. This is suggestive of a radical anion ligand in the excited state which provides a convenient spectroscopic marker for the dmp radical anion. The mixed ligand excited state can be thought of as $[(Ph_3P)_2Cu^{II}(dmp^-)]^{+*}$. However, assignment of a localized excited state for the homoleptic complex, $[(dmp)Cu^{II}(dmp^-)]^{+*}$, was incomplete since no features of the MLCT state were observed.

In subsequent experiments by McGarvey and coworkers, stronger experimental evidence was presented in support of a localized excited state [51]. Pulsed laser excitation of a MeOH solution of $Cu^{I}(dmp)_2^+$ at 416 nm produced Raman bands at 1598, 1503, 1426, 1295, and 1315 cm^{-1}, attributable to scattering from the ground state. The same experiment performed in CH_2Cl_2 reveals some marked differences. The band at 1503 cm^{-1} shows increased intensity while the two bands in the 1300 cm^{-1} region show a decreased intensity. Moving the excitation energy further into the red, 447 nm, produces bands with the same frequencies but different intensities in MeOH. In CH_2Cl_2, 447 nm excitation yields no features in the 1300 cm^{-1} region. The intensities of those bands resemble the bands that are present in the mixed ligand complex, $Cu^{I}(dmp)(PPh_3)_2^+$, from the first series of TR^3 experiments, suggesting resonant scattering from a radical anion centered transition (Table 2). This is the strongest evidence in support of a localized excited state, $[(dmp)Cu^{II}(dmp^{-1})]^{+*}$.

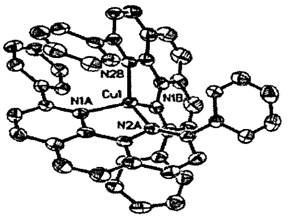
3.3. $Cu^{I}(dpp)_2^+$

Analogous to $Cu^{I}(dmp)_2^{+*}$, $Cu^{I}(dpp)_2^{+*}$ also exhibits ambient temperature photoluminescence in CH_2Cl_2 solution [59]. However, in more polar Lewis basic organic solvents and in water, $Cu^{I}(dpp)_2^{+*}$ emits light while $Cu^{I}(dmp)_2^{+*}$ does not. $Cu^{I}(dpp)_2^+$ is the first cuprous bisphenanthroline derivative to display r.t. PL in solvents other than dichloromethane [59]. This result was rationalized through the phenyl substituents, which serve to effectively shield the metal center from exciplex formation. Quenching studies were performed by McMillin et al. on both $Cu^{I}(dmp)_2^{+*}$ and $Cu^{I}(dpp)_2^{+*}$ in CH_2Cl_2 using pyridine as a quencher [55].

They reported a Stern–Volmer quenching constant, K_{SV}, of 80 M^{-1} for $Cu^{I}(dmp)_2^{+*}$ and no quenching of $Cu^{I}(dpp)_2^{+*}$ by pyridine, lending further support



$Cu^{I}(dpp)_2^+$



$Cu^{II}(dpp)_2^{2+}$

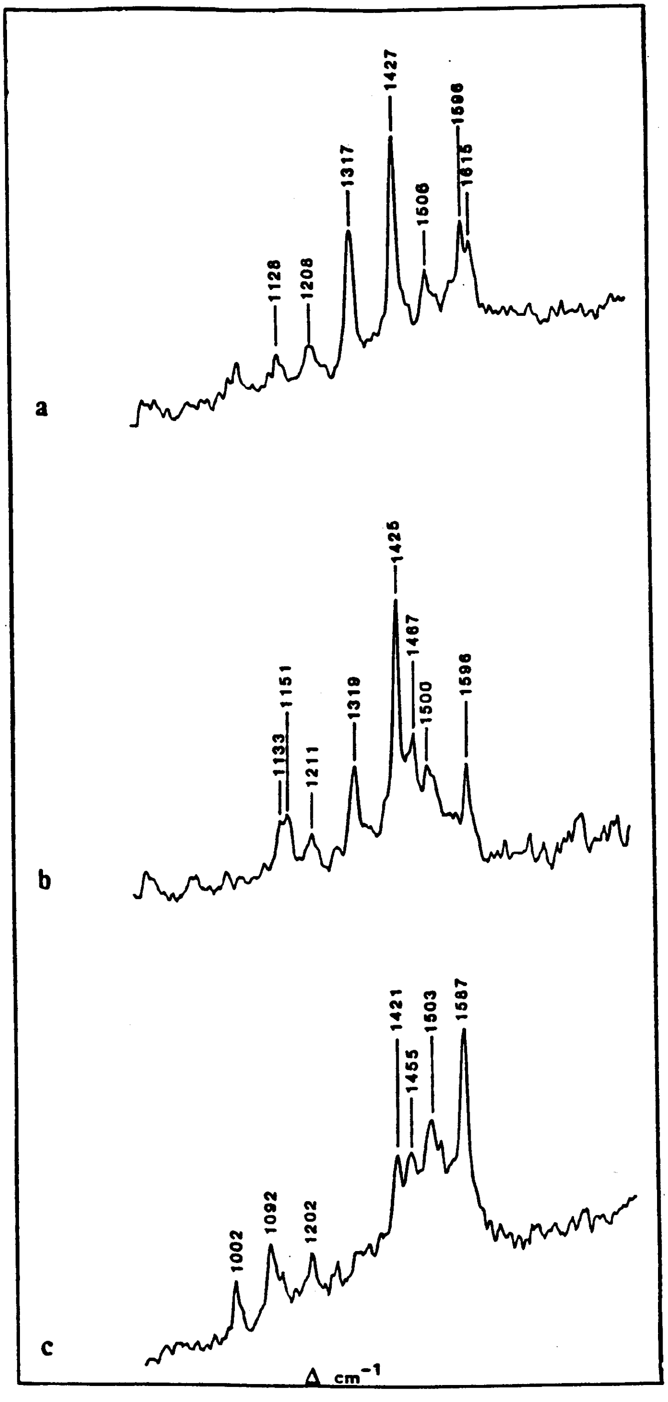


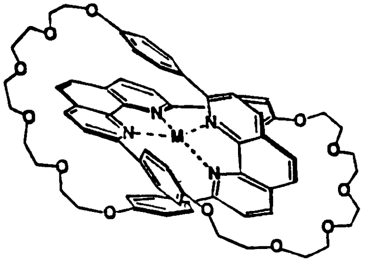
Fig. 4. Resonance Raman spectra of $Cu^I(dmp)_2^+$ in MeOH (spectrum a) and CH_2Cl_2 (spectrum b) and of $Cu^I(dmp)(PPh_3)_2^+$ in MeOH (spectrum c). All samples were argon saturated and excited at 355 nm.

Table 2
Frequencies (cm^{-1}) observed in TR^3 spectra of Cu(I) phenanthroline compouds

$Cu^I(dmp)_2^+(MeOH)$	$Cu^I(dmp)_2^+(CH_2Cl_2)$	$Cu^I(dmp)(PPh_3)_2^+(MeOH)$
1026		1002
		1092
1128	1133	
	1151	
1208	1211	1202
		1265
1317	1320	
1427	1425	1421
	1467	1455
1509	1500	1503
		1531
1596	1596	1587
1615		

to the notion of steric shielding of the metal center by the phenyl rings. Furthermore, crystal structures of both $Cu^I(dpp)_2^+$ and $Cu^{II}(dpp)_2^{2+}$ shows both oxidation states to be four-coordinate in the solid state [25].

Catenanes are macrocyclic molecules that have interlocking molecular rings. The work of Sauvage et al. has focused on the synthetic development of catenanes based on dpp derivatives with substituents in the *para* position of the phenyl rings. Cu(I) catenanes display photophysical properties comparable to those of $Cu^I(dpp)_2^{+*}$ [60–63]. Varying the number of atoms in the molecular knot seems to have a variable effect on the excited state lifetime. This can be attributed to an increase, or decrease, in the flexibility of the knot as the formally Cu(II) center tetragonally distorts away from pseudo-tetrahedral geometry in the excited state [60–63].



3.4. $Cu^I(2,9\text{-}(R)_2\text{-}phen)_2^+$ and $Cu^I(2,9\text{-}(R)_2\text{-}4,7\text{-}(R')_2\text{-}phen)_2^+$

A recent paper by McMillin et al. reported the effects of 2,9 disubstitution on the excited state properties of $Cu^I(phen')_2^+$ systems [26]. A variety of alkyl substituents were employed including methyl, *n*-butyl, *n*-octyl, neopentyl, and *sec*-butyl groups. They report photophysical data in deoxygenated CH_2Cl_2 solution for the series of homoleptic bischelates of Cu(I). The PLI_{max} shifts to shorter wavelengths in the order dmp > d*n*bp > d*n*op > dnpp > d*s*bp. This trend is attributed to the increasing steric bulk at the 2- and 9-positions of the phen moiety, which decreases the amount of D_2 flattening the phen ligands can attain with respect to one another in the cupric state. An interesting observation is that the dnpp derivative has a shorter excited state lifetime than does the d*s*bp derivative [26]. One might think the opposite was true since the dnpp ligand has more steric bulk than the d*s*bp ligand does. However, the d*s*bp occupies a greater spatial region proximate to the metal center than does the dnpp, in which the steric bulk originates at the β carbon.

Karpishin et al. have synthesized and characterized $Cu^I(bfp)_2^+$, where bfp = 2,9-bis(trifluoromethyl)-1,10-phenanthroline [65]. They found that addition of the highly electron withdrawing trifluoromethyl groups dramatically perturbs the electronic structure of the copper complex and enhance it's ability to act as a photooxidant relative to $Cu^I(dmp)_2^+$. The steric and electronic influence of the trifluormethyl groups leads to an excited state lifetime of almost twice that of $Cu^I(dmp)_2^+$, $\tau = 165$ ns in CH_2Cl_2 and a blue shifted PLI_{max} at 665 nm. The emission quantum yield is also higher than that of $Cu^I(dmp)_2^+$, with a value of 3.3×10^{-3}. To date, the compound has the largest metal-based reduction for a Cu(I) bis-phenanthroline compound, $E_{1/2}$ ($Cu^{II/I}$) = 1550 mV versus SCE [65].

The effects of electronic delocalization on the photophysical properties of Cu(I) complexes using a variety of derivitized phenanthroline ligands was reported recently by Karpishin et al. [64]. The ligands include dop (2,9-di-(2-methylphenyl)-1,10-phen), xop (2-(2-methylphenyl)-9-(2,6-dimethylphenyl)-1,10-phen, dpep (2,9-diphenylethynyl-1,10-phen) and dmesp (2,9-dimesityl-1,10-phen), shown for clarity in Fig. 1. Ground state absorption spectra of $Cu^I(dop)_2^+$, $Cu^I(xop)_2^+$, $Cu^I(dmesp)(dpp)^+$, and $Cu^I(dpp)_2^+$ reveal a low energy shoulder, which is thought to be a reflection of the degree of distortion away from D_{2d} symmetry. Measurements of oscillator strengths were consistent with the degree of π delocalization, decreasing in the order: $Cu^I(dmesp)(dpp)^+ > Cu^I(dpp)_2^+ > Cu^I(dop)_2^+ > Cu^I(xop)_2^+$. The rate constant for non-radiative decay, $k_{nr,}$ increased in the order: $Cu^I(dpp)_2^+ < Cu^I(dop)_2^+ < Cu^I(xop)_2^+$. Both the xop and dop complexes displayed higher energy PLI_{max} than did the dpp derivative, yet both have higher non-radiative decay rate constant values and shorter excited state lifetimes. They concluded that π delocalization was primarily responsible for their observations [64].

The first isolated heteroleptic copper bis-phenanthroline compound, $Cu^I(dtbp)(dmp)^+$, where dtbp = 2,9-di-*tert*-butyl-1,10-phenanthroline, was reported recently by Karpishin et al. [29]. Due to the lability of first-row transition metals, heteroleptic copper compounds are difficult to prepare, and hence, the ligands are expected to scramble. However, the formation of $Cu^I(dtbp)_2^+$ is sterically difficult, and the heteroleptic $Cu^I(dtbp)(dmp)^+$ is stabilized. The sheer steric bulk of the two *t*-butyl groups help to keep the metal center in a rigid coordination sphere, leading to a large degree of destabilization of the cupric state. This molecular tuning of excited state properties leads to a Cu(I) coordination compound that possesses a long lived excited state, $\tau_{es} = 730$ ns, and high emission quantum yield, $\phi_{em} = 0.01$ [29]. Table 3 shows pertinent photophysical data for various cuprous bis-phenanthroline compounds in dichloromethane solution.

3.5. Correlations of spectroscopic energies and redox potentials

A notable and expected characteristic of $(d\pi)^6$ polypyridyl MLCT excited states is the linear correlation between E_{abs} or E_{em} and $\Delta E_{1/2}$ for a homologous series of complexes, as given by Eqs. (8) and (9) [5–8]. Here, E_{abs} and E_{em} are the energies for the maximum of the absorption and emission spectrum, respectively.

$$E_{\mathrm{abs}} = \Delta E_{1/2} + \lambda \tag{8}$$

$$E_{\mathrm{em}} = \Delta E_{1/2} - \lambda \tag{9}$$

$\Delta E_{1/2}$ can be calculated using Eq. (10),

$$\Delta E_{1/2} = E_{1/2}(\mathrm{M}^{n+/(n-1)+}) - E_{1/2}(\mathrm{L}^{0/-}) \tag{10}$$

where $E_{1/2}(\mathrm{M}^{n+/(n-1)+})$ is the reduction potential of the metal center and $E_{1/2}(\mathrm{L}^{0/-})$ is the first ligand reduction potential, generally measured by cyclic voltammetry. Plots of E_{abs} and E_{em} versus $\Delta E_{1/2}$, using data reported for $\mathrm{Cu^I(phen')_2^+}$ compounds in nominally non-coordinating $\mathrm{CH_2Cl_2}$ solution, are shown in Fig. 5. The absorption and emission energies of the Cu(I) compounds are almost independent of $\Delta E_{1/2}$. In marked contrast, Ru(II) and Os(II) complexes display a strong dependence [4]. This is a significant observation in that it points to a fundamental difference between Cu(I) and Ru(II) chromophores. Typically, the $\mathrm{Ru^{III/II}}$ and $\mathrm{L}^{0/-}$ redox couples approach electrochemical and chemical reversibility at the electrode surface. This is not true for $\mathrm{Cu^I(phen')_2^+}$, as discussed in Section 2. There are significant inner-sphere geometric changes associated with the oxidation of Cu(I) to Cu(II) and the redox process is not strictly reversible. Therefore, incorporated within $\Delta E_{1/2}$ values for $\mathrm{Cu^I(phen')_2^+}$ systems are the energetics associated with

Table 3
Electrochemical properties of $\mathrm{Cu^I(phen')_2^+}$ at room temperature

Compound[a]	$\mathrm{Cu^{II/I}}$ (V)[b]	$\mathrm{(phen')^{0/-}}$ (V)[c]	$\Delta E_{1/2}$ (V)[d]	E_{em} (V)[e]
$\mathrm{Cu^I(phen)_2^+}$	0.19	−1.40	1.59	–
$\mathrm{Cu^I(dmp)_2^+}$	0.50[f]	−2.18[f,g]	2.68	1.68
$\mathrm{Cu^I(dpp)_2^+}$	0.37[f]	−2.21[f,g]	2.58	1.73
$\mathrm{Cu^I(bfp)_2^+}$	1.55	−1.22	2.77	1.87
$\mathrm{Cu^I(tptap)_2^+}$	0.93[f]	−1.51	2.43	1.73
$\mathrm{Cu^I(dipp)_2^+}$	0.59[f]	−2.21[f,g]	2.80	1.82
$\mathrm{Cu^I(d}s\mathrm{bp)_2^+}$	0.68[f]	−2.19[f,g]	2.87	1.80
$\mathrm{Cu^I(dop)_2^+}$	1.00	−1.86[g]	2.69	1.84
$\mathrm{Cu^I(xop)_2^+}$	1.03	−1.56[g]	2.59	1.84

[a] Same as in Table 1, all compounds were the $\mathrm{PF_6^-}$ salts and were measured in this electrolyte.

[b] All potentials are versus SCE unless otherwise noted.

[c] Ligand reductions.

[d] $\Delta E_{1/2}$ values calculated using Eq. (10) in the text.

[e] Emission maximum in eV.

[f] Potentials versus ferrocene.

[g] Measured in $\mathrm{CH_3CN}$.

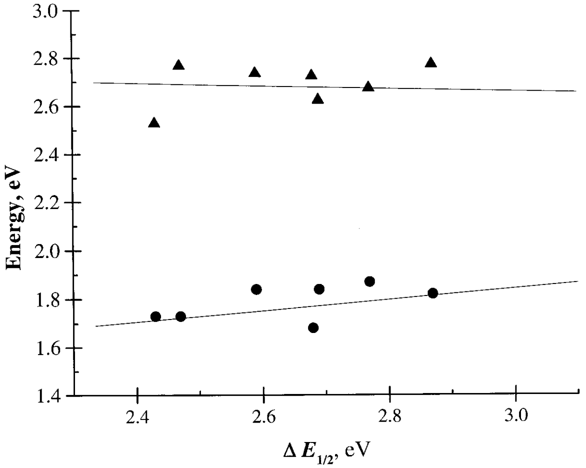


Fig. 5. The energy of the MLCT absorption maxima (triangles) and the emission maxima (circles) in electron volts plotted versus the difference in the ligand based and metal based reduction potentials in electron volts, $\Delta E_{1/2}$, as defined by Eq. (10). The spectral data and metal based reduction potentials were obtained in dichloromethane solution.

tortional distortion and coordination number changes that are not relevant to light absorption, which is a vertical process. The example cited earlier, where the $\mathrm{Cu^{II/I}(dmp)_2^{2+/+}}$ reduction potential was tuned over 300 mV by varying the solvent from CH_2Cl_2 to DMSO, Fig. 2, without a significant change in the absorption maximum in each solvent, is an excellent example of this. One might expect a better correlation between $\Delta E_{1/2}$ and E_{em}, and this may be the case from the data shown. However, a larger data set is needed before any possible correlation can be quantified fully.

3.6. Excited state decay

Excited state decay processes that occur from thermally equilibrated MLCT excited states are well understood for $(d\pi)^6$ polypyridyl complexes of Ru(II), Os(II), and Re(I) [5–8]. In these chromophores excited state decay occurs with retention of stereochemistry and coordination number and the parameters that influence excited state decay have been extensively studied [5–8]. The factors that influence the excited state decay dynamics in $\mathrm{[(phen)Cu^{II}(phen^{-})]^{+*}}$ compounds are anticipated to be more complex than those described for $(d\pi)^6$ polypyridyl chromophores. The structural and coordination number changes inherent in Cu(I) choromophores give rise to a number of potential energy surfaces that may participate in radiative and non-radiative decay. Examination of available photophysical data given in Table 1 for $\mathrm{Cu^{I}(phen')_2^{+*}}$, in the context of radiative and non-radiative decay theory, is revealing. These observations are discussed below.

Excited state relaxation with emission of a photon is an important decay pathway in $\mathrm{Cu^{I}(phen')_2^{+*}}$ compounds. Following Strickler, k_r may be evaluated by Eq. (11),

$$k_r = 8\pi hcn^3 < \nu^{-3} >^{-1} B \tag{11}$$

where B is the Einstein transition probability of absorption into the emitting state, n is the refractive index of the medium, h is Planck's constant, c is the speed of light, and $< \nu^{-3} >^{-1}$ is the inverse of the cube of the emission energy, ν^{-3} [66]. B is related to the transition moment dipole, d, by Eq. (12).

$$B = (8\pi^3/3h^2c) < d >^2 \tag{12}$$

Eq. (11) predicts plots of k_r versus $< \nu^{-3} >^{-1}$ should be linear. The plots of k_r versus $< \nu^{-3} >^{-1}$ using the data in Table 1 for $\mathrm{Cu^I(phen')_2^+}$ and data for $\mathrm{Cu^I(phen')(PPh_3)_2^+}$ are shown in Fig. 6. The quality of the correlation is surprisingly good given the small data set that is available and the estimated errors in the determination of k_r. The data suggest that $< d >$ may be similar between the $\mathrm{Cu^I(phen')_2^+}$ and the $\mathrm{Cu^I(phen')(PPh_3)_2^+}$ families of compounds.

An important feature of MLCT excited states are correlations between the rate constants for non-radiative decay and the emission maxima for a homologous series of complexes. The Energy Gap Law for excited state decay is a qualitative description stating that the lifetime of an emissive excited state increases with increased emission energy [5]. A terse examination of the photophysical data for $\mathrm{Cu^I(phen')_2^+}$ (and $\mathrm{Cu^I(phen')(PPh_3)_2^+}$) show clearly that the observed excited state lifetimes do increase with the emission energy in a manner exactly analogous to that described for other systems (Fig. 6).

Non-radiative decay theory has been described in detail elsewhere [67]. Briefly, non-radiative relaxation is the process where the excited state decays to the ground state releasing the excess electronic energy into the vibrational and solvent modes of the ground state [67]. There are many acceptor modes that mediate the transition, however in the limit where the accepting modes can be approximated as an averaged single mode, the rate constant for non-radiative decay is given by Eq. (13),

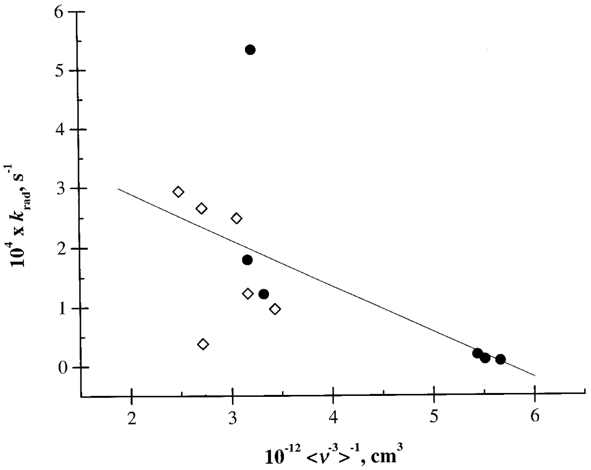


Fig. 6. Plots of the radiative rate constant, k_{nr}, versus the inverse cube of the emission maximum frequency for $\mathrm{Cu^I(phen')_2^{+*}}$ (diamonds) and $\mathrm{Cu^I(phen')(PPh_3)_2^{+*}}$ (circles) in dichloromethane solution.

$$\ln(k_{\mathrm{nr}}) = \ln(\beta_0) + \ln(FCWD) \tag{13}$$

where β_0 is the vibrationally induced electronic coupling term, and $(FCWD)$ is the Franck Condon weighted density of states given by Eq. (14),

$$\ln(FCWD) = -\frac{1}{2}\ln(\hbar\omega E_0) - S - \frac{\gamma E_0}{\hbar\omega} + \left(\frac{\gamma+1}{\hbar\omega}\right)^2 \left(\frac{(\Delta\bar{\nu}_{1/2})^2}{16\ln 2}\right)^2 \tag{14}$$

where S is the Huang–Rhys factor or the electron vibrational coupling constant, γ is $\ln(E_0/S\hbar\omega) - 1$ and $\Delta\nu_{1/2}$ is the bandwidth which contains the solvent reorganization energy and the low-frequency modes treated classically. Eq. (14) is valid in the weak coupling limit, $\hbar\omega \gg k_{\mathrm{b}}T$, and assumes the vibronic spacings ($\hbar\omega$) of the excited state are the same as those for the ground state. In this limit, the $\ln(FCWD)$ can be determined from a line-shape analysis of the emission spectra and this is useful for abstracting the relationships between E_0, S, and $\hbar\omega$ [67].

Plots of $\ln(k_{\mathrm{nr}} \times 1\mathrm{s})$ versus E_{em} are shown in Fig. 7 for $\mathrm{Cu^I(phen')_2^+}$ and $\mathrm{Cu^I(phen')(PPh_3)_2^+}$, along with published data for $\mathrm{Os^{II}(phen)L_4}$ for comparative purposes. Slopes and intercepts from a linear regression analysis of the data in Fig. 7, as well as comparative data for other MLCT excited states, are given in Table 4. Examination of the data in Fig. 6 shows that the quality of the $\ln(k_{\mathrm{nr}} \times 1\mathrm{s})$ versus E_{em} plots, or energy gap correlations, are remarkably good given the size of the data sets. The dependence of k_{nr} on E_{em} for the $\mathrm{Cu^I(phen')_2^+}$ is seen to parallel that found for $\mathrm{Os^{II}(phen)L_4}$. The data suggest that the energies of the averaged accepting modes and the magnitudes of β_0 may be comparable on going from $\mathrm{Cu^I(phen')_2^+}$ to $\mathrm{Os^{II}(phen)L_4}$ [68]. If true, this is an important observation because it suggests that non-radiative relaxation in $\mathrm{Cu^I(phen')_2^{+*}}$ is dictated by similar factors to those already elucidated in polypyridyl complexes of Ru(II), Os(II) and

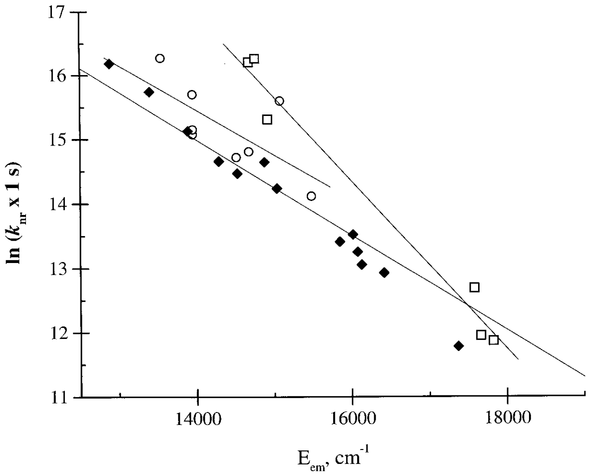


Fig. 7. Plots of the natural logarithm of the non-radiative rate constant, k_{nr}, versus the emission maximum, E_{em}, in wavenumbers for $\mathrm{Cu^I(phen')_2^{+*}}$ (diamonds) and $\mathrm{Cu^I(phen')(PPh_3)_2^{+*}}$ (circles) in dichloromethane solution and $\mathrm{Os^{II}(phen')L_4^{2+*}}$ compounds (squares).

Re(I). The correlation of $\ln(k_{nr} \times 1s)$ versus E_{em} for $Cu^{I}(phen')(PPh_3)_2^+$ is less well defined. The slope and intercept are dictated by the two clusters of data at the extrema. The slopes derived from the energy gap plots of $Cu^{I}(phen')(PPh_3)_2^+$ are seen to be similar in magnitude to $[(CO)_3Re^{I}(bpy)L]^+$ [69]. The importance of this analysis is that the data points to how non-chromophoric ligands influence k_{nr}.

Electronic delocalization of the excited electron in an MLCT excited state results in longer excited state lifetimes [70,71]. This feature is extremely important in designing chromophores that emit light in the red with long-lived excited states. Recent studies involving synthetic modification of the acceptor ligands to maximize electronic delocalization have been presented for $Cu^{I}(phen')_2^+$ systems [64]. For excited states, delocalization of the excited electron over a larger ligand framework is argued to reduce the magnitude of the Huang–Rhys factor S. From Eq. (14), a reduction in S should decrease the magnitude of the vibrational overlap factors and enhance lifetimes. Further studies are required to exploit this feature and develop near-infrared emitters with long lifetimes.

4. Summary

Shown in Scheme 1 is the proposed model for cuprous phenanthroline MLCT excited state relaxation in non-coordinating solvents. Process A represents the absorption of a UV–vis photon to populate the MLCT excited state. The symmetry about the metal center in the Franck–Condon state is necessarily that of the ground state but whether it is best described as D_{2d} or D_2 remains unknown [72,73]. The multiplicity of the Franck–Condon state is necessarily a singlet and it vibrationally relaxes to a lower energy state, i.e. undergo a Jahn–Teller distortion. This step is represented by process B in Scheme 1 and has not been time resolved. The vibrational relaxation appears to be accompanied by a change in multiplicity, giving the excited state triplet character. This excited state stabilization is responsible for the significant red shift in the emission spectra with respect to the ground state absorption spectra. The red shifted emission is strong evidence that the absorbing and emitting states are not the same.

Table 4
Slopes for plots $\ln k_{nr}$ versus E_{em}

Compounds	$\delta(\ln k_{nr} \times 1s)/\delta(E_{em})$ (10^3 cm)	Intercept
.$[Ru(bpy)_2L_2]^{2+}$	-0.9[a]	–
$[Os(bpy,phen)L_4^{2+}$	-0.9[b]	25
$[(CO)_3Re(bpy)L]^+$	-1.5[c]	–
$[Cu(phen')_2]^+$	-0.7[d]	25
$[Cu(phen')(PPh_3)_2]^+$	-1.3[d]	35

[a] J.V. Caspar, T.J. Meyer, Inorg. Chem. 22 (1983) 2444.

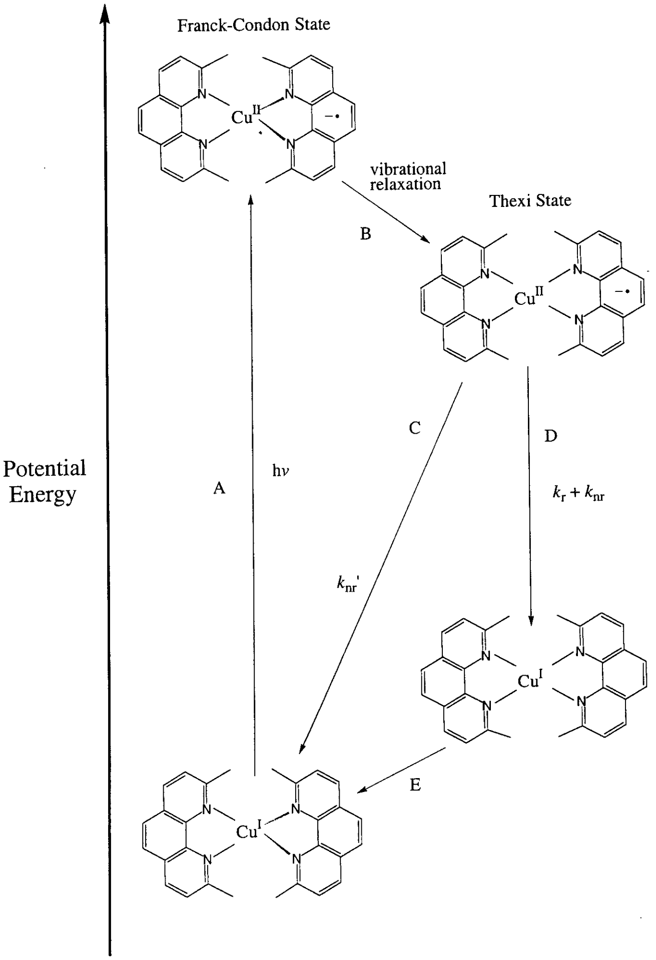
[b] E.M. Kober, J.V. Caspar, R.S. Lumpkin, T.J. Meyer, J. Phys. Chem. 90 (1986) 3722.

[c] J.V. Caspar, T.J. Meyer. J., Phys. Chem. 87 (1983) 952.

[d] This work.

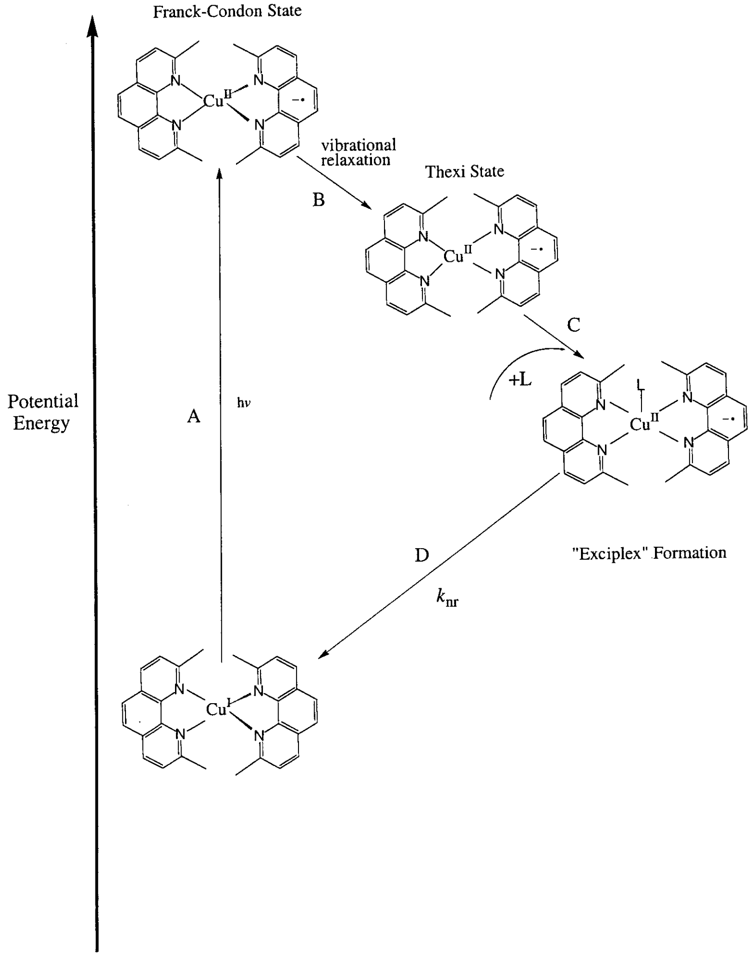
In CH_2Cl_2 solution, the product of relaxation is the thermally equilibrated MLCT excited state, which for $Cu^I(dmp)_2^{+*}$ is comprised of two states separated in energy by ≈ 1800 cm^{-1} [58]. At r.t., these states are in equilibrium and radiative and nonradiative decay rate constants are 2.71×10^3 and 1.18×10^7 s^{-1}, respectively. Radiative relaxation is vertical in the Franck–Condon sense and the ground state product possesses the same nuclear coordinates of the relaxed MLCT excited state. Therefore, radiative decay yields a geometrically unfavored complex that then distorts to the ground state minima by a process that has not been observed, step D in Scheme 1. Nonradiative decay directly to the ground state, step C, or by alternative pathways, steps D and E, are both probable.

The proposed model for cuprous bis-phenanthroline MLCT excited state relaxation in coordinating solvents is shown in Scheme 2. The first two processes, light



Scheme 1.

absorption, step A, and vibrational relaxation, step B, are the same as in Scheme 1. The fundamental difference in the models proposed for excited state relaxation in coordinating and non-coordinating solvents is exciplex formation, step C in Scheme 2. The Cu(II) center adopts a higher coordination number as the exciplex forms. Addition of a fifth ligand is formally a second-order process and the lifetime of the four-coordinate excited state thus depends on the concentration of incoming ligand, denoted as L. Process D represents the non-radiative relaxation of the exciplex back to ground state products. Mechanistic details of this process are currently lacking. In principle, the process could occur by concerted or step-wise mechanisms and could even involve radiative decay. However, to date, only short-lived MLCT excited states have been observed.



Scheme 2.

5. Conclusions

Cu(I) bis-phenanthrolines are fascinating complexes that possess rich and varied photophysical properties. A fundamental understanding of the excited state spectroscopy and dynamics are now evolving. These studies have demonstrated that the MLCT excited states have attractive properties that make them useful as chromophores for excited state electron and energy transfer [17,24,74]. The photophysical properties of $Cu^{I}(phen')_2^+$ systems parallel those observed in $(d\pi)^6$ chromophores and appear to be behave as expected based on non-radiative decay theory.

Large inner sphere and coordination number changes are a novel property of these excited states that give rise to distinct behaviors such as the large energy shifts between absorption and emission and the creation of open coordination sites upon light absorption. The large excited state distortions and changes in coordination geometry may provide a further test for existing non-radiative decay theories such as the Energy Gap Law [67].

The outlook for future research of Cu(I) bis-phenanthroline compounds appears to be very good. Some possible future directions are given below.

1. A quantitative analysis of emission spectral data using Franck–Condon lineshape fitting protocols to yield information regarding inner sphere and solvent reorganization energies. This analysis would also be useful in understanding how changes in chromophoric and non-chromophoric ligands influence excited state decay. In this regard, the use of weakly coordinating anions would increase solubility in aromatic and hydrocarbon solvents where emission is likely to be observed [75].
2. Application of Heller theory to Raman data would be revealing in understanding how stretching and tortional modes mediate excited-state relaxation [76].
3. Excited state decay via exciplex or solvent addition to $Cu^{I}(phen')_2^{+*}$ excited states is a rare example of this behavior in transition metal systems [53–55]. Exciplexes are short lived and have not yet been detected spectroscopically for these Cu(I) phenanthroline chromophores. Details regarding exciplex formation are badly needed and could be observed by time resolved vibrational spectroscopies.
4. The exploitation of $Cu^{I}(phen')_2^+$ compounds in photocatalysis [77], solar energy conversion [78], chemical sensing [38], and as molecular probes in biology[79] deserves further development.
5. Cu(I) bis-phenanthroline chromophores may be used to photoinitiate electron transfer reactions and study subsequent charge recombination through large structural barriers [74]. In this manner, electron transfer dynamics which are accompanied by substantial inner sphere reorganization can be quantified on short time scales to test existing electron transfer theories.

Acknowledgements

We thank the National Science Foundation (CHE-9708222) and the ACS-PRF (34427-AC3) for support of this work.

References

[1] V. Balzani, F. Scandola, Supramolecular Photochemistry, Horwood, Chichester, 1991.
[2] D.M. Roundhill, J.P. Fackler (Eds). Optoelectronic Properties of Inorganic Compounds, Plenum, New York, 1999.
[3] J.I. Steinfeld, An Introduction to Modern Molecular Spectroscopy: Molecules and Radiation, MIT, Cambridge, 1974.
[4] P.Y. Chen, T.J. Meyer, Chem. Rev. 98 (1998) 1439.
[5] K. Kalyanasundaaram, Coord. Chem. Rev. 46 (1982) 159.
[6] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. Von Zelewsky, Coord. Chem. Rev. 84 (1988) 85.
[7] T.J. Meyer, Acc. Chem. Res. 22 (1989) 163.
[8] G.A. Crosby, J. Chem. Ed. 60 (1983) 791.
[9] B. O'Regan, M. Gratzel, Nature 353 (1991) 737.
[10] W. Xu, R.C. McDonough, B. Langsdorf, J.N. Demas, B.A. DeGraff, Anal. Chem. 66 (1994) 4133.
[11] Y.I. Kim, S. Salim, M.J. Huq, T.E. Mallouk, J. Am. Chem. Soc. 113 (1991) 9561.
[12] J.R. Lakowicz, H. Malak, I. Gryczynski, F.N. Castellano, G.J. Meyer, Biospectroscopy 1 (1995) 163.
[13] H.D. Gafney, Coord. Chem. Rev. 104 (1990) 113.
[14] Chem. & Eng. News. 77 (March 1, 1999) 39.
[15] M. Gratzel, private communication.
[16] (a) C. Kutal, Coord. Chem. Rev. 99 (1990) 213. (b) O. Horvath, Coord. Chem. Rev. 135 (1994) 303.
[17] M. Ruthkosky, C.A. Kelly, F.N. Castellano, G.J. Meyer, Coord. Chem. Rev. 171 (1998) 309.
[18] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, Wiley Interscience, New York, 1988, pp. 755–776.
[19] P.J. Burke, D.R. McMillin, W.R. Robinson, Inorg. Chem. 19 (1980) 1211.
[20] R. Hamalainen, M. Ahlgren, U. Terpeinen, T. Raikas, Cryst. Struct. Commun. 8 (1979) 75.
[21] P.J. Burke, K. Henrick, D.R. McMillin, Inorg. Chem. 21 (1982) 1881.
[22] F.K. Klemens, C.E. Palmer, S.M. Rolland, P.E. Fanwick, D.R. McMillin, J.P. Sauvage, New J. Chem. 14 (1990) 129.
[23] A.J. Pallenberg, K.S. Koenig, D.M. Barnhart, Inorg. Chem. 34 (1995) 2833.
[24] M. Ruthkosky, F.N. Castellano, G.J. Meyer, Inorg. Chem. 35 (1996) 6406.
[25] M.T. Miller, P.K. Gantzel, T.B. Karpishin, Inorg. Chem. 37 (1998) 2285.
[26] K.S. Koenig, A.J. Pallenburg, M.K. Eggleston, D.R. McMillin, Inorg. Chem. 36 (1997) 172.
[27] M. Ruthkosky, G.J. Meyer, unpublished results.
[28] Y. Jahng, J. Hazdrigg, D. Kimball, E. Riesgo, R.R. Thummel, Inorg. Chem. 36 (1997) 5390.
[29] M.T. Miller, P.K. Gantzel, T.B. Karpishin, J. Am. Chem. Soc. 121 (1999) 4292.
[30] F.S. Stephens, P.A. Tucker, J. Chem. Soc., Dalton Trans. (1973) 2293.
[31] F.S. Stephens, J. Chem. Soc., Dalton Trans. (1972) 1350.
[32] J. Kaiser, G. Brauer, F.A. Schroder, I.F. Taylor, S.E. Rasmussen, J. Chem. Soc., Dalton Trans. (1974) 1490.
[33] W.D. Harrison, D.M. Kennedy, M. Power, R. Sheahan, B.J. Hathaway, J. Chem. Soc., Dalton Trans. (1981) 1556.
[34] W.D. Harrison, B.J. Hathaway, D. Kennedy, Acta Crystallogr., Sect. B 35 (1979) 2301.
[35] W.D. Harrison, B.J. Hathaway, Acta Crystallogr., Sect. B 35 (1979) 2910.
[36] R.J. Fereday, P. Hodgson, S. Tyagi, B.J. Hathaway, J. Chem. Soc., Dalton Trans. (1981) 2070.
[37] O.P. Anderson, Inorg. Chem. 14 (1975) 730.
[38] D. Tran, B.W. Skelton, A.H. White, L.E. Laverman, P.C. Ford, Inorg. Chem. 37 (1998) 2505.
[39] J. Gazo, I.B. Bersuker, J. Garaj, M. Kabesoa, J. Kohout, H. Langfelderova, M. Melnik, M. Serator, F. Valach, Coord. Chem. Rev. 19 (1976) 253.
[40] I.M. Proctor, F.S. Stephens, J. Chem. Soc. A (1969) 1248.
[41] H. Nakai, Bull. Chem. Soc. Jpn. 44 (1971) 2412.
[42] M.B. Ferrari, G.G. Fava, C. Pellizzi, J. Chem. Soc., Chem. Commun. (1977) 8.

[43] J. Foley, S. Tyagi, B.J. Hathaway, J. Chem. Soc., Dalton Trans. (1984) 1.
[44] B.R. James, J.P. Williams, J. Chem. Soc. (1961) 2007.
[45] M. Ruthkosky, D.V. Scaltrito, C.A. Kelly, G.J. Meyer, in preparation.
[46] A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, Wiley Interscience, New York, 1980.
[47] H. Irving, J.P. Williams, J. Chem. Soc. (1953) 3192.
[48] (a) M.T. Buckner, D.R. McMillin, J. Chem. Soc., Chem. Comm. (1979) 759. (b) M.T. Buckner, T.G. Matthews, F.E. Lytle, D.R. McMillin, J. Am. Chem. Soc. 101 (1979) 5846. (c) G. Blasse, D.R. McMillin, Chem. Phys. Lett. 70 (1978) 1.
[49] M.W. Blaskie, D.R. McMillin, Inorg. Chem. 19 (1980) 3519.
[50] J.J. McGarvey, S.E.J. Bell, K.C. Gordon, Inorg. Chem. 27 (1988) 4003.
[51] K.C. Gordon, J.J. McGarvey, Inorg. Chem. 30 (1991) 2986.
[52] J. Lackowicz, Principles of Fluorescence Spectroscopy, Plenum, New York, 1983.
[53] E.M. Stacy, D.R. McMillin, Inorg. Chem. 29 (1990) 393.
[54] R.M. Everly, D.R. McMillin, Photochem. Photobiol. 50 (1989) 2902.
[55] S.G. Kruglik, V.A. Galievsky, V.S. Chirvony, P.A. Apanasevich, V.V. Ermolenkov, V.A. Orlovich, L. Chinsky, P.Y. Turpin, J. Phys. Chem. 99 (1995) 5732.
[56] C.E.A. Palmer, D.R. McMillin, C. Kirmaier, D. Holten, Inorg. Chem. 26 (1987) 3167.
[57] D.R. Crane, P.C. Ford, J. Am. Chem. Soc. 113 (1991) 8510.
[58] J.R. Kirchoff, R.E. Gamache, M.W. Blaskie, A.A. Del Paggio, R.K. Lengel, D.R. McMillin, Inorg. Chem. 22 (1983) 2380.
[59] C.O. Dietrich-Buchecker, P.A. Marnot, J.P. Sauvage, J.R. Kirchoff, D.R. McMillin, J. Chem. Soc., Chem. Commun. (1983) 513.
[60] A.K.I. Gunhurst, D.R. McMillin, C.O. Dietrich-Buchecker, J.P. Sauvage, Inorg. Chem. 28 (1989) 4070.
[61] P. Ferderlin, J.M. Kern, A. Rasteger, C.O. Dietrich-Buchecker, P.A. Marnot, J.P. Sauvage, New. J. Chem. 14 (1990) 9.
[62] C.O. Dietrich-Buchecker, J.F. Nierengarten, J.P. Sauvage, N. Armaroli, V. Balzani, L. DeCola, J. Am. Chem. Soc. 115 (1993) 11237.
[63] N. Armaroli, M.A.J. Rodgers, P. Ceroni, V. Balzani, C.O. Dietrich-Buchecker, J.M. Kern, A. Bailal, J.P. Sauvage, Chem. Phys. Lett. 241 (1995) 555.
[64] M.T. Miller, P.K. Gantzel, T.B. Karpishin, Inorg. Chem. 37 (1999) 3414.
[65] M.T. Miller, P.K. Gantzel, T.B. Karpishin, Angew. Chem. Int. Ed. Eng. 37 (1998) 1556.
[66] S.J. Strickler, R.A. Berg, J. Chem. Phys. 37 (1962) 814.
[67] K.F. Freed, J. Jortner, J. Chem. Phys. 52 (1970) 6272.
[68] E.M. Kober, J.V. Caspar, R.S. Lumpkin, T.J. Meyer, J. Phys. Chem. 90 (1986) 3722.
[69] J.V. Caspar, T.J. Meyer, J. Phys. Chem. 87 (1983) 952.
[70] G.F. Strouse, J.R. Schoonover, R. Duesing, S. Boyde, W.E. Jones, T.J. Meyer, Inorg. Chem. 34 (1995) 473.
[71] N.H. Damrauer, T.R. Boussie, M. Devenney, J.K. McCusker, J. Am. Chem. Soc. 119 (1997) 8253.
[72] W.L. Parker, G.A. Crosby, J. Phys. Chem. 93 (1989) 5692.
[73] R.M. Everly, D.R. McMillin, J. Phys. Chem. 95 (1991) 9071.
[74] M. Ruthkosky, C.A. Kelly, M.C. Zaros, G.J. Meyer, J. Am. Chem. Soc. 119 (1997) 12004.
[75] S.H. Strauss, Chem. Rev. 93 (1993) 927.
[76] (a) A.B. Myers, Chem. Rev. 96 (1996) 911. (b) A.B. Myers, Acc. Chem. Res. 30 (1997) 519.
[77] P.A. Breddels, G. Blassie, D.J. Casadonte, D.R. McMillin, Ber. Bunsenges. Phys. Chem. 88 (1984) 572.
[78] N. Alonso-Vante, J.F. Nierengarten, J.P. Sauvage, J. Chem. Soc., Dalton Trans. (1994) 1649.
[79] D.R. McMillin, K.M. McNett, Chem. Rev. 98 (1998) 1201.