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A Chromophore–Quencher Complex Incorporating a Photoredox-Active Ligand

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A photoredox-active ligand (CL), the chromophore–quencher complexes $\mathrm{Cu(CL)(CF_3SO_3)_2}$ (**1**) and $\mathrm{Cu(CL)(H_2O)_2(CF_3SO_3)_2}$ (**2**), where CL = 4,7-di-*n*-butoxy-1,3-bis((3′-pyridylmethyl)imino)isoindoline, and the reference complexes $\mathrm{Cu(L)(H_2O)(CF_3SO_3)_2}$ (**3**), where L = 1,3-bis((3′-pyridylmethyl)imino)isoindoline, and $\mathrm{Zn(CL)(H_2O)_2(ClO_4)_2}$ (**4**) have been synthesized and characterized. The ligand CL is subject to a protonation equilibrium with ground state $\mathrm{p}K_\mathrm{a} = 8.99 \pm 0.06$ and an approximate excited-state $\mathrm{p}K_\mathrm{a} = 10.5 \pm 0.5$. In 4:1 acetonitrile:water, the excited ligand CL* at pH > 13.5 has $\lambda_\mathrm{em} = 419$ nm ($\phi_\mathrm{em} = 0.19$), while the excited protonated ligand $\mathrm{CLH^{+*}}$ at pH < 7 has $\lambda_\mathrm{em} = 486$ nm ($\phi_\mathrm{em} = 0.86$). In hexane the lifetime of the fluorescent excited state of CL was determined to be 2.00 ± 0.07 ns. In "dry" acetonitrile the emission came from both CL* and $\mathrm{CLH^{+*}}$ but only one decay was resolved with $\tau = 2.64 \pm 0.03$ ns. Picosecond transient absorption spectroscopy and emission decay studies of CL in 4:1 acetonitrile:water solution showed an absorption feature ($\lambda_\mathrm{max} = 625$ nm and $\tau = 9.6 \pm 0.6$ ns) which is assigned to $\mathrm{CLH^{+*}}$ in an extensive hydrogen-bonding solvation network. Oxidative quenching of CL* by methyl viologen dication, *p*-benzoquinone, or $\mathrm{Co(bpy)_3^{3+}}$ in acetonitrile generated a common transient absorbance centered at 480 nm ($\epsilon \approx 6000\ \mathrm{M^{-1}\ cm^{-1}}$) which is assigned to the cation radical $\mathrm{CL^+}$. Picosecond absorption spectroscopy of the zinc reference complex **4** showed an absorption feature ($\lambda_\mathrm{max} = 625$ nm) similar to that seen for CL in 4:1 acetonitrile: water and assigned to $\mathrm{CLH^{+*}}$. Excitation of **4** results in emission with $\lambda_\mathrm{em} = 486$ nm ($\phi_\mathrm{em} = 0.92$) and $\tau = 9.3 \pm 0.3$ ns. While the chromophore–quencher complexes **1** and **2** show the same emission band as that seen for **4**, the quantum yields and lifetimes of this emission are much reduced ($\phi_\mathrm{em} = 0.03$, $\tau = 3.14 \pm 0.04$ ns and $\phi_\mathrm{em} = 0.22$, $\tau = 4.2 \pm 0.1$ ns, respectively). Transient absorption studies of **1** and **2** both display oxidative quenching of the chromophore by Cu(II) as evidenced by the generation of cation radical $\mathrm{CL^+}$ absorbance. The charge separated state for both complexes is formed in less than 25 ps and decays with a lifetime of approximately 300 ps. The difference in forward and backward electron-transfer rates is attributed to Marcus inverted region behavior.

Introduction

Research in the area of electron transfer in chromophore–quencher complexes has focused mainly on the factors that govern the rates of electron transfer such as the separation of donor and acceptor, the thermodynamic driving force and inverted region behavior, inner- and outer-sphere reorganizational energies, and the orientation of donor and acceptor.[1] We are interested in the design of a chromophore–quencher complex in which the photoinduced charge-separated state may exhibit metal-centered chemistry. Our ultimate goal is to exploit these complexes as photocatalysts for the activation of small molecules of industrial importance.

Several studies have been carried out on purely organic donor–acceptor systems and include electron-transfer quenching of the pulse radiolysis generated biphenyl radical anion,[2] pyrene or anthracene excited states,[3] 1,4-dimethoxyanthrene excited state,[4] and porphyrin excited state.[5] Metal to ligand charge transfer (MLCT) based excited states have been shown to be quenched intramolecularly by either oxidative or reductive process.[6] Few studies have shown definitively the intramolecular quenching of an organic chromophore excited state by a metal ion. One such study[7] involves electron transfer from a porphyrin-based excited state to a Ru(III) polypyridyl quencher covalently linked exocyclic to the porphyrin. Another study[8] has shown that the first excited singlet state of the anthryl chromophore can be quenched by a Co(III) cage complex provided that the link between the two species is sufficiently large enough to eliminate an energy-transfer interaction involving the short-lived Co(III) triplet state. This energy-transfer process has been previously shown[9] in $\mathrm{[(NH_3)_5Co(III)(TSC)]^{2+}}$ (TSC is *trans*-4-stilbenecarboxylate), where it was concluded that intramolecular excitation energy transfer from the excited state of the chromophore to a low-lying nonspectroscopic triplet LMCT state is responsible for the observed photoreduction of Co(III). More recently, a similar Co(III) system was investigated[10] using a naphthyl group as the chromophore and efficient electron-transfer quenching was observed at large distances across a flexible peptide spacer with an inverse distance relationship. The authors suggested that a hydrogen-

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bonding interaction between the peptide and a coordinated ammonia ligand provides a pathway for electron transfer between donor and acceptor.

The use of an organic chromophore centered on the ligand offers several advantages over metal-centered chromophores. Organic chromophores generally have much higher absorptivities and would thus be more efficient photocatalysts. A chromophore which is pseudostable as a radical is desired and many such organic chromophores exist. Most importantly, the different bonding and substitutional properties of the metal (M/M^-) couple would be accessible for chemistry without affecting the nature of the chromophore. The chromophore used in this study is an alkoxy derivative of the highly fluorescent 2,3-dicyanohydroquinone molecule which has been cyclized to form a substituted diiminoisoindole chromophore and then functionalized with methylpyridyl moieties to facilitate coordination to a metal ion and eliminate ground-state coupling of the chromophore and metal. The choice of metal ion used to form a chromophore quencher complex which exhibits intramolecular electron transfer must ensure that the complex formed does not possess a CT transition with sufficient spectral overlap with the chromophore emission to quench the excited state by an energy-transfer mechanism. Additionally, the complex must be thermodynamically and photochemically stable enough to be isolated in pure form.

Here we present a study of intramolecular electron transfer in a chromophore–quencher complex which possesses the desired aforementioned properties. Synthetic modifications of the ligand can be used in future work to enhance the efficiency of formation and increase the lifetime of the charge-separated state so that the chemistry of the reduced metal site quencher can be explored.

Experimental Section

Physical Measurements. UV–vis spectra were recorded on a Cary 5 spectrophotometer. Fluorescence spectra were recorded on a Perkin-Elmer 204-S fluorescence spectrometer. Fluorescence quantum yields were calculated by using a 5×10^{-3} M quinine sulfate in 1 N H_2SO_4 solution ($\phi = 0.508$) as a standard.[11] Quantum yields were corrected[12] for the difference in refractive index between the standard and the solution being measured. Infrared spectra of sample KBr pellets were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 200-MHz or a Bruker AMX 400-MHz NMR spectrometer. H-NMR chemical shifts were reference to TMS at 0.0 ppm, and ^{13}C-NMR chemical shifts were referenced to solvent carbon ($CDCl_3$, 77.0 ppm). Cyclic voltammetry was performed using a BAS Model CV-27 cyclic voltammograph. Details of the electrochemical cell have been previously described.[13] Experiments were performed in dry acetonitrile[14] (0.1 M tetrabutylammonium hexafluorophosphate, TBAH, or 0.1 M tetrabutylammonium tetrafluoroborate, TBAT), at 25 °C, with a three-electrode system consisting of platinum-disk working (BAS 1.6-mm diameter), platinum-wire counter, and silver wire quasi-reference electrodes. Ferrocene ($E° = 400$ mV vs NHE) was used as an internal reference.[15] Picosecond transient absorption spectroscopy was performed at the Canadian Centre for Picosecond Laser Flash Photolysis at Concordia University for which a detailed description of the laser system has been given.[16] A passively mode-locked Nd:YAG laser provided ≈30-ps (fwhm) pulses (2–3 mJ/pulse) at 355 nm for excitation and two YAG amplifiers and a solution of phosphoric acid in D_2O was used to generate a probe continuum. Emission lifetimes were determined by exciting the sample with a 30-ps (fwhm) pulse (0.2 mJ/pulse) at 355 nm from the passively mode-locked Nd:YAG laser. The emission was passed through a 400-nm cutoff filter and appropriate neutral density filters before entering a Hamamatsu C979 temporal disperser and a C1000 streak camera. A C1097 delay unit was used to trigger the camera between 1 and 8 ns from the excitation pulse by splitting the beam and passing a portion of the pulse into a Hamamatsu C1083 photodiode. Appropriate blank runs of acetonitrile solvent and acetonitrile solutions of the quenchers used to generate the cation radical spectrum of CL showed no transient absorbance between 425 and 675 nm. The ligand L was also examined and was found to have no transient absorption in the region of interest. Lifetime data was fitted by using Sigma Plot Scientific Graphing System, version 4.02, from Jandel Corp. and is reported to ±1 standard deviation.

Reagents. 2,3-Dicyano-1,4-hydroquinone, ammonium hexafluorophosphate, 1,3-diiminoisoindoline, *n*-bromobutane, *p*-benzoquinone, methyl viologen dichloride, and 3-(aminomethyl)pyridine were obtained from Aldrich. NH_3 and argon were obtained from Air Products. Caledon HPLC grade acetonitrile was used for cyclic voltammetry and picosecond transient absorption spectroscopy. Reagent grade solvents used were distilled and dried when required.[17] $Cu(CF_3SO_3)_2 \cdot nH_2O$ was prepared as previously,[18] and methyl viologen dihexafluorophosphate was prepared by metathesis of the chloride salt with ammonium hexafluorophosphate in water.

Synthesis. 1,4-Di-*n*-butoxy-2,3-dicyanobenzene (A) was prepared analogously to the dimethyl ether.[19] A 9.6-g amount of 2,3-dicyanohydroquinone (0.06 mol) was added to a mixture of 38.5 mL of *n*-bromobutane (0.36 mol) and 20.7 g of K_2CO_3 (0.15 mol) in 200 mL of DMF, and the resulting suspension was rapidly stirred at 25 °C for 120 h. The solution was poured into 500 mL of water and filtered, and the flocculant white precipitate was washed with 2 L of water. Recrystallization from ethanol followed by vacuum drying at 110 °C for 10 h afforded 14.68 g of shiny white platelets (yield, 90%): mp 182–3 °C; ^{1}H NMR ($CDCl_3$) 7.21 (s, 2 H), 4.08 (t, 4 H), 1.82 (quint, 4 H), 1.52 (sext, 4 H), 0.98 (t, 6 H); ^{13}C NMR ($CDCl_3$) 155.2, 118.4, 113.1, 105.2, 69.9, 30.9, 19.0, 13.7. Anal. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.76; H, 7.18; N, 10.43.

4,7-Di-*n*-butoxy-1,3-diiminoisoindoline (B) was prepared in a similar manner to 1,3-diiminoisoindoline.[20] An 8.6-g amount of **A** (0.032 mol) and 0.2 g of Na (0.008 mol) were dissolved in 500 mL of methanol and brought to reflux. NH_3 was bubbled into the solution until saturated and then continuously at a slow rate while the solution was refluxed for 12 days. The solution was then cooled and the product filtered off. Recrystallization from 1:1 acetone:diethyl ether followed by vacuum drying for 12 h at 25 °C afforded 7.5 g of off-white needles (yield, 81%): mp 228 °C dec; ^{1}H NMR ($CDCl_3$) 8.19 (br s, 2 H), 6.92 (s, 2 H), 4.07 (t, 4 H), 1.83 (quint, 4 H), 1.51 (sext, 4 H), 0.98 (t, 6 H); ^{13}C NMR ($CDCl_3$) 167.4, 149.3, 120.8, 115.9, 68.5, 31.1, 19.3, 13.8. Anal. Calcd for $C_{16}H_{23}N_3O_2$: C, 66.41; H, 8.01; N, 14.52. Found: C, 65.86; H, 7.88; N, 14.26.

4,7-Di-*n*-butoxy-1,3-bis((3′-pyridylmethyl)imino)isoindoline (CL) was prepared similarly to other 1,3-disubstituted isoindolines.[21] A 20-mL volume of 3-(aminomethyl)pyridine (0.15 mol) was vacuum distilled (2 Torr, 90 °C) into a flask containing 4.22 g of **B** (0.015 mol) and 90 mL of anhydrous ethanol. The solution was slowly heated to reflux. The NH_3 produced was removed by the application of vacuum and an argon purge at 15-min intervals for the first 3 h. The solution was refluxed for a further 9 h and then cooled. The solution was poured into 600 mL of rapidly stirred water and placed in the fridge for 2 h. The flocculant pale yellow suspension was filtered out and washed with 500 mL of water. Vacuum drying at 25 °C for 16 h produces a green glassy mass, which can be ground to a powder and recrystallized from diethyl ether to give 4.40 g of yellow to light green powder which is very hygroscopic (yield, 64%): mp 67 °C dec; ^{1}H NMR ($CDCl_3$) 8.69 (s, 2 H), 8.52 (d, 2 H), 7.90 (d, 2 H), 7.27 (t, 2 H), 6.94 (s, 2 H), 5.04 (s, 4 H), 4.14 (t, 4 H), 1.78 (quint, 4 H), 1.40 (sext, 4 H), 0.90 (t, 6 H); ^{13}C NMR ($CDCl_3$) 166.9, 149.7, 149.5, 148.7, 148.4, 135.7, 123.4, 118.4, 116.6, 69.1, 49.6, 31.2, 19.2, 13.8. Anal. Calcd for $C_{28}H_{33}N_5O_2 \cdot 5H_2O$: C, 70.11; H, 7.00; N, 14.60. Found: C, 70.10; H, 6.85; N, 14.59.

1,3-Bis((3′-pyridylmethyl)imino)isoindoline (L) was prepared from 1,3-diiminoisoindoline by a similar method to that used for **CL** (yield, 89%): mp 165–6 °C; ^{1}H NMR ($CDCl_3$) 8.64 (s, 2 H), 8.48 (s, 2 H),

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7.77 (d, 2 H), 7.43 (s, 2 H), 7.23 (mult, 3 H), 6.79 (s, 2 H), 5.02 (br s, 4 H); ^{13}C NMR ($CDCl_3$) 168.6, 149.7, 149.6, 148.3, 136.9, 136.5, 130.4, 123.7, 121.9, 50.3 (cis), 44.9 (trans). Anal. Calcd for $C_{20}H_{17}N_5$: C, 73.37; H, 5.23; N, 21.39. Found: C, 73.17; H, 5.20; N, 21.72.

$Cu(CL)(CF_3SO_3)_2$ (1). A 1.03-g amount of $Cu(CF_3SO_3)_2 \cdot nH_2O$ (2 mmol based on $n = 6$) was added to a solution of 1.06 g of **CL** (2 mmol) in 140 mL of ethanol. The solution was stirred in the dark at 25 °C for 42 h. Filtration of the light green precipitate followed by two recrystallizations from acetonitrile with diethyl ether diffusion gave 0.56 g of olive needles. These were rinsed with diethyl ether and vacuum dried at 110 °C for 8 h (yield, 27%). IR: coordinated CF_3SO_3, ν_4 at 1220, 1241, 1282 cm^{-1}. Anal. Calcd for $C_{30}H_{33}N_5O_8S_2F_6Cu$: C, 43.24; H, 3.99; N, 8.40. Found: C, 43.87, H, 4.13; N, 8.56.

$Cu(CL)(H_2O)_2(CF_3SO_3)_2$ (2) can be isolated if ether is diffused into the filtrate from the above complex. Filtration, rinsing with diethyl ether, and vacuum drying at 110 °C for 8 h gave 0.29 g of pale green crystals (yield, 12%). IR: coordinated CF_3SO_3, ν_4 at 1223, 1245, 1281 cm^{-1}; coordinated H_2O, 3491 cm^{-1} (s). Anal. Calcd for $C_{30}H_{37}N_5O_{10}S_2F_6Cu$: C, 41.45; H, 4.29; N, 8.06. Found: C, 41.51; H, 4.13; N, 8.10.

If **2** is repeatedly recrystallized as for **1**, **2** loses coordinated water and is converted to **1**.

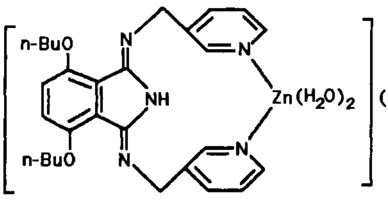
$Cu(L)(H_2O)(CF_3SO_3)_2$ (3). A 1.61-g amount of $Cu(CF_3SO_3)_2 \cdot nH_2O$ (3.4 mmol based on $n = 6$) was added to a solution of 1.25 g of **L** (3.8 mmol) in 180 mL of 95% ethanol. The pale blue slurry was stirred at 25 °C for 20 h and collected by filtration. The precipitate was placed in 10:1 acetonitrile:water and heated gently until the solid dissolved and the solution became dark blue. The solution was cooled and filtered, and diethyl ether was diffused into the filtrate. A 0.65-g amount of dark blue crystals deposited after 2 days. These were rinsed with diethyl ether and vacuum dried for 16 h at room temperature (yield, 27%). IR: coordinated CF_3SO_3, ν_4 at 1226, 1249, 1278 cm^{-1}; coordinated H_2O, 3532 cm^{-1} (s). Anal. Calcd for $C_{22}H_{19}N_5O_7S_2F_6Cu$: C, 37.37; H, 2.71; N, 9.90. Found: C, 37.43; H, 3.11; N, 10.04.

$Zn(CL)(H_2O)_2(ClO_4)_2$ (4). A solution of 0.35 g of $Zn(ClO_4)_2 \cdot 6H_2O$ (0.9 mmol) in 25 mL of acetone was added dropwise to a stirred solution of 0.63 g of **CL** (.13 mmol) in 50 mL of acetone. The light yellow precipitate that forms immediately was collected by filtration and recrystallized twice from acetonitrile with diethyl ether diffusion. The light yellow microcrystalline powder was rinsed with diethyl ether and vacuum dried at room temperature for 16 h (yield, 61%). IR: coordinated H_2O, 3524 cm^{-1} (s); ionic ClO_4, ν_3 at 1098 cm^{-1} (s), ν_4 at 929 cm^{-1} (w). Anal. Calcd for $C_{28}H_{37}N_5O_{12}Cl_2Zn$: C, 43.57; H, 4.83; N, 9.07. Found: C, 43.67; H, 4.47; N, 9.04. ^1H NMR ($CDCl_3$): CL protons, 8.72 (s, 2 H), 8.49 (d, 2 H), 8.09 (d, 2 H), 7.58 (t, 2 H), 7.29 (s, 2 H), 5.05 (s, 4 H), 4.25 (t, 4 H), 1.79 (quint, 4 H), 1.40 (sext, 4 H), 0.92 (t, 6 H); coordinated water, 8.94 (broad s, 4 H).

Results and Discussion

Chromophore Ligand and Complex Characterization. Although a crystal structure determination of one of the complexes was not possible, a reasonably unambiguous case for the coordination mode of the chromophore ligand CL to Zn(II) and Cu(II) ions can be made on the basis of NMR, IR, and UV–vis spectroscopies.

The ^1H-NMR spectra of the free chromophore ligand CL and the ligand L are very simple and are consistent with a plane of symmetry bisecting each molecule. Thus for CL, only the proton resonances of one type of butyl, one methylene, and one pyridine group are observed. The same spectrum for CL, albeit slightly broadened, is seen in the ^1H-NMR spectrum of **4** suggesting that CL's plane of symmetry is not lost upon coordination to Zn(II). This can only occur if CL is bidentate and coordinates to Zn(II) via the pyridine nitrogens.



The possibility that CL could also coordinate via its indole nitrogen can be discounted since molecular modeling of the tridentate coordination mode showed severe steric strain. The solid-state IR spectrum of **4** showed the perchlorate ions to possess tetrahedral symmetry and are therefore not coordinated to Zn(II). In acetonitrile, the coordinated water molecules of **4** may be expected to exchange rapidly with solvent due to the rather large rate constant for this process.[22] Nevertheless, the greater thermodynamic stability of the diaquo complex is shown by its isolation from acetonitrile solution.

The solid-state IR spectra of the three copper complexes and the zinc complex display several features that are supportive of a common coordination mode for the ligands L and CL. The pyridine ring C–H stretching vibrations that appear at 3048 and 3018 cm^{-1} for CL and 3052 and 3025 cm^{-1} for L are shifted to higher energies in all four complexes. The pyridine C=C stretching mode that appears at 1567 and 1572 cm^{-1} for CL and L, respectively, is also shifted by 35–45 cm^{-1} in the complexes. Both of these shifts are known[23] to be indicative of the coordination of pyridines. Additional shifts are expected for the out-of-plane and the in-plane pyridine ring bending modes which occur in the range 1020–1030 and 625–640 cm^{-1}, respectively. In **4**, the in-plane ring bending mode is shifted to 657 cm^{-1}, but in all the copper complexes, this mode and the out-of-plane mode are obscured by other more intense absorptions.

The indole N–H bending mode at 1490 cm^{-1} is relatively unchanged in the complexes compared to the free ligand as is the ether C–O stretch at 1064 cm^{-1}, which can only be observed in the copper triflate complexes due to the intense perchlorate absorption of the zinc complex. In addition, the indole N–H stretching mode observed at around 3400 cm^{-1} in the free ligands is still observed in the complexes although it is shifted by 120 cm^{-1} to lower frequencies.

Due to the substitutional lability of Cu(II), it is difficult to know the exact composition of the Cu(II) coordination sphere in the solvated complex. The solution IR spectra of the copper complexes in acetonitrile display only two $\nu_4(SO_3)$ modes at 1272 and 1225 cm^{-1}, which are characteristic of free triflate.[24–26] The vacant coordination sites about Cu(II) are presumably occupied by solvent molecules, either acetonitrile and/or water. The electronic spectrum of **1** in acetonitrile displays one ligand field transition at 568 nm (Table 1). For CuN_{4-6} chromophores the suggested stereochemistry for a single unresolved band of this energy is tetragonally distorted octahedral.[27] In the case of **2**, the band at 616 nm with a shoulder at 840 nm suggests a square pyrimidal structure. For **3**, one broad band at 579 nm also suggests a tetragonally distorted octahedral structure. The difference in coordination geometries between the chromophore–quencher complexes **1** and **2** are the result of the coordination of water in **2**. This difference has a significant effect on the electrochemical and transient absorption studies to follow.

Ground- and Excited-State Protonation. The electronic absorption spectra of L and the chromophore ligand CL in acetonitrile are shown in Figure 1a,b. The absorptions at wavelengths less than 320 nm are assigned to $\pi \rightarrow \pi^*$ transitions of the pyridine and benzene moieties. The absorption centered at 367 nm in the spectrum of CL but not of L is assigned to a

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Table 1. Electroic Absorbance UV–Vis Data[a] for Complexes and Ligands

CL	1	2	4	L	3	assgnt
204 (4.85)	200 (4.44)	200 (4.56)	200 (4.01)	226 (4.73)	229 (3.93)	π,π^{*c}
223 (4.71)	235 (4.15)	233 (4.33)	231 (3.66)			π,π^{*c}
262 (4.45)	246 (4.14)	243[g] (4.30)	243[g] (3.61)			π,π^{*c}
268 (4.45)	270 (4.03)	270 (4.24)	269 (3.52)	263 (4.50)	263 (3.68)	π,π^{*c}
282 (4.37)	283 (4.02)	282[g] (4.21)	284 (3.52)			π,π^{*c}
	294[g] (3.90)	294[g] (4.09)	297[g] (3.38)	298[g] (4.09)	308 (4.11)	π,π^{*c}
				321[g] (4.07)	320[g] (3.21)	π,π^{*c}
367 (4.06)	367[g] (3.45)	365[g] (3.72)	365[g] (3.01)			nb,π^{*d}
418[g] (3.87)	420 (3.83)	414 (3.93)	419 (3.29)			nb,π^{*e}
	568[b] (1.82)	616[b] (1.79)			579[b] (1.72)	d,d[f]
		840[b] (1.28)				d,d[f]

[a] Wavelength in nm (log ε) for 1×10^{-4} M solutions in acetonitrile. [b] 1×10^{-2} M solutions. [c] Ligand-centered transitions. [d] Due to neutral form of ligand. [e] Due to protonated form of ligand. [f] Ligand field transition. [g] Shoulder.

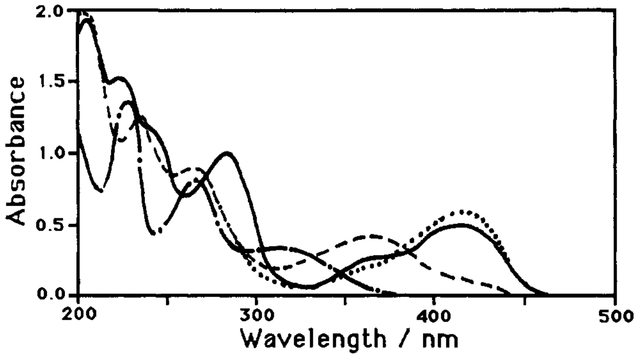

Figure 1. UV–vis spectra of (a) L (– • –), (b) CL (---), (c) CLH^+ (···), and (d) $Cu(CL)(CF_3SO_3)_2$ (—) in acetonitrile solutions of 1×10^{-4} M concentration.

nb→π* transition arising from the interaction of the ether oxygen lone pairs with the isoindoline π system. It is this transition that is responsible for the excited-state properties of CL. The slight shoulder seen at longer wavelengths is not observed in rigorously anhydrous tetrahydrofuran and is dramatically enhanced upon the addition of glacial acetic acid (Figure 1c). A ground-state protonation equilibrium is proposed

$$CL + H^+ \rightleftharpoons CLH^+$$

involving the indole or imine nitrogens of CL. A spectroscopic titration of the ligand in 4:1 acetonitrile:water solution yielded a pK_a of 8.99 ± 0.06. The visible absorption spectra of complexes **1** (Figure 1d), **2**, and **4** are nearly identical to CLH^+ (Figure 1c) and suggest that, in the ground state, protonation of coordinated CL ligand is nearly complete. For **1** in 4:1 acetonitrile:water, complete conversion to **2** occurs within 5 min and the complex appears stable only within the pH range 5.5–9.3. Bearing in mind these limitations, both complex **1** and **2** gave an extrapolated pK_a of 9.4. The ease of protonation of coordinated compared to free CL is due in part to the greater acidity of water bound to a M^{2+} metal ion. A similar effect of added cations enhancing the rate of solvent-assisted protonation has been previously observed in azaphenanthrenes.[28]

The fluorescence spectrum of CL in 4:1 acetonitrile:water is also sensitive to the presence of protons in solution. At a pH of 13.48 (Figure 2a), emission occurs from the excited state of unprotonated CL with $\lambda_{max} = 419$ nm and $\phi_{em} = 0.19$. As the pH of the solution is lowered, the intensity of the 419-nm band decreases and a band at 486 nm begins to grow in until at a pH < 7 (Figure 2b) only the band at 486 nm ($\phi_{em} = 0.86$) is observed. This lower energy emission is derived from a protonated excited state of the ligand, and the pK_a^* has been estimated as 15.6 using a Forster cycle analysis[29] or 10.5 ± 0.5 from the inflection point in the fluorometric titration curve.[30] The large increase in the quantum yield of emission upon protonation contradicts the energy gap law for radiationless transition rates and probably results from a more structurally constrained molecule upon protonation. This would reduce the vibrational and rotational modes responsible for radiationless deactivation of the excited state. The absence of a large Stokes shift suggests that the ground state is extensively hydrogen bonded,[31] and this is supported by the observation of a slightly decreased Stokes shift in hydrogen-bonding solvents such as ethanol, where the emission λ_{max} is 481 nm for CLH^{+*} and 431 nm for CL^*. This effect is also seen in studies of the transient absorption spectroscopy of CL to follow.

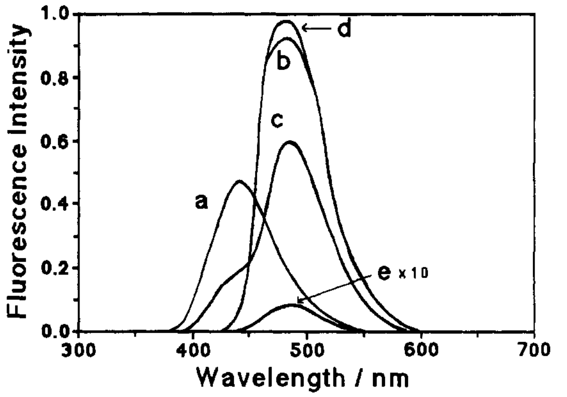

Figure 2. Apparent fluorescence emission spectra of (a) CL at a pH of 13.48, (b) CL at a pH of 6.94, (c) CL, (d) $Zn(CL)(H_2O)_2(ClO_4)_2$, and (e) $Cu(CL)(CF_3SO_3)_2$. Spectra (a) and (b) were recorded at 1×10^{-4} M in 4:1 acetonitrile:water. Spectra (c)–(e) were recorded in acetonitrile solutions of 1×10^{-4} M concentration. The relative emission intensity of (e) has been multiplied by a factor of 10. The excitation wavelength is 365 nm.

In neat acetonitrile solution (Figure 2c), the fluorescence spectrum of CL is intermediate between that of the protonated and neutral forms (65:35, respectively). Rigorous drying of the solvent ($[H_2O] < 10^{-3}$ M) gives a slight reduction in the intensity of the low-energy emission and an accompanying smaller increase in the intensity of the high-energy emission. If the concentration of the ligand is increased to more than 5×10^{-3} M, self-absorption effects decrease the intensity of the 486-nm emission and completely eliminate the 419-nm emission. It should also be noted that only the high-energy emission is observed in aprotic solvents that can be made sufficiently water free to prevent significant protonation of CL^*.[32]

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(28) Marzazacco, C. J.; Deckey, G.; Colarulli, R.; Siuzdak, G.; Halpern, A. M. *J. Phys. Chem.* **1989**, *93*, 2935.

(29) Weller, A. *Prog. React. Kinet.* **1961**, *1*, 189.

(30) There are many examples of poor agreement between Forster cycle pK_a^* values and those obtained by fluorescence intensity titrations. The Forster cycle calculation is expected to be in error when either the (0–0) transition energies of acid and base forms cannot be measured accurately or the solvent behaves in a nonideal manner (see: Ireland, J. F.; Wyatt, P. A. H. *Adv. Phys. Org. Chem.* **1976**, *12*, 131). A kinetic determination of pK_a^* is complicated by the nonequilibrium conditions which exist in the excited state.

(31) Sharma, K. S.; Bhushan, K.; Singh, G. P. *J. Photochem. Photobiol., A: Chem.* **1990**, *52*, 473.

The protonation equilibria that exists in the ground and excited states for both free and coordinated CL in acetonitrile solution is an added complexity that interferes with the interpretation of electron-transfer processes. Nevertheless, the solubility and stability of the chromophore–quencher complexes made acetonitrile the most suitable solvent for this investigation.

The fluorescence spectrum for **4** (Figure 2d) shows only the 486-nm emission ($\phi = 0.92$) due to the protonated excited state. The same emission is seen for **1** (Figure 2e) and **2** but at reduced intensity ($\phi = 0.03$ and 0.22, respectively). This dramatic loss in fluorescence quantum yield may be due to quenching by one or more of several different mechanisms.[33] These include (i) electronic energy transfer, (ii) electron transfer, (iii) a chemical reaction involving atom transfer, (iv) exciplex formation, (v) spin-catalyzed deactivation, and (vi) the external heavy atom effect. In cases where the observed rate constants are greater than 10^7 s^{-1}, consideration of only the electron- and energy-transfer processes is warranted.[34] Both the radiative and radiationless (or Coulombic) energy-transfer mechanisms require spectral overlap between the emission of the donor and the absorption of the acceptor.[35] The lowest energy LMCT transition for the copper–pyridyl complexes prepared in this study cannot be resolved from the more intense ligand bands but is expected to occur in the 250–330-nm region by analogy with other Cu(II)–N-heterocycle complexes[36] thus eliminating the possibility that energy transfer is operative here. Energy transfer to a ligand field excited state by an exchange mechanism[37] would be very inefficient due to the change in symmetry and multiplicity required and has been estimated[38] as 2×10^{-4} s^{-1} for this system. Intramolecular electron-transfer quenching of the chromophore ligand CL by Cu(II) appears to be the only mechanism available to account for the observed results.

The cyclic voltammetry of CL and the complexes **1** and **2** in "dry" acetonitrile solution showed the electrode reactions to be electrochemically irreversible. The oxidation potential of CL is expected to be less than the value of +1.58 V vs NHE reported for *p*-dimethoxybenzene[39] and was found to occur with an anodic peak potential of +1.40 V vs NHE at a scan rate of 20 mV/s. As the scan rate was increased, the peak potential shifted anodically, and if it was decreased, then the peak became ill-defined. Glacial acetic acid was added to an acetonitrile solution of CL to attempt the determination of the oxidation potential of CLH^+. Nothing was observed up to the anodic limit of 2.1 V. The CL oxidation potential was unchanged in the chromophore–quencher complexes, but an additional cathodic wave was observed which is assigned to the Cu(II/I) couple. The position of the cathodic wave for this couple occurred at –0.5 and –0.75 V at a scan rate of 20 mV/s for complex **1** and **2**, respectively. The difference in Cu(II/I) couples must be related to the coordination of water and the effect this has on the geometry and composition of the Cu(II) coordination sphere.

An estimate of the reducing power of the excited state of CL can be derived from the ground-state oxidation couple minus the energy of emission between excited- and ground-state zeroth vibrational levels. For CL, ($\lambda_{em}(0–0) = 3.26$ V), $CL^{+/*} = -1.86$ V. For CLH^+ only the lower limit of $CLH^{2+/+} \geq 2.1$ V could be determined. Since $\lambda_{em}(0–0) = 2.77$ V for CLH^+, this gives an estimated value of $CLH^{2+/+*} \geq -0.67$ V. The protonated excited state is a far weaker reductant than CL^* and is probably electron-transfer inactive as will be shown in the transient absorption studies of the chromophore–quencher complexes.

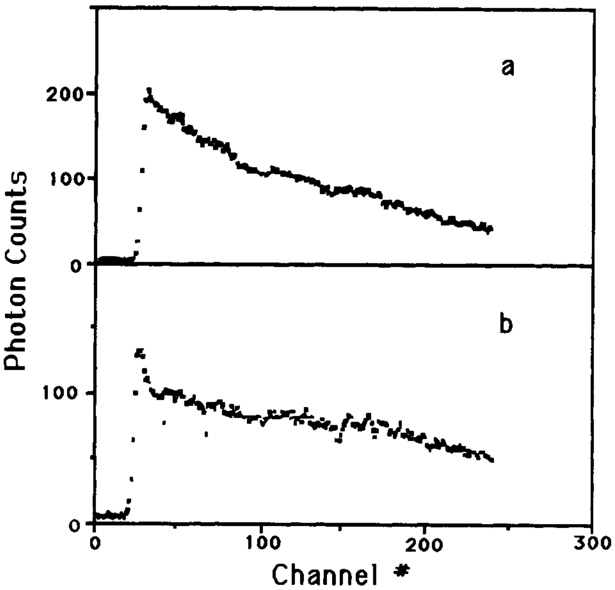

Figure 3. Emission decay data with a streak camera speed of 26.6 ps/channel of (a) CL, 2.8×10^{-4} M in acetonitrile, and (b) CL, 2.0×10^{-4} M in 4:1 acetonitrile:H_2O.

Ligand Excited-State Emission and Transient Absorption. For CL in hexane, the excited-state lifetime was determined to be 2.00 ± 0.07 ns. In neat acetonitrile (Figure 3a), biphasic behavior was expected due to the emissive decay of both CL and CLH^+ excited states, but only one decay could be resolved ($\tau = 2.64 \pm 0.03$). When water is added to acetonitrile (Figure 3b), a significant enhancement of CLH^{+*} lifetime is observed ($\tau = 6.7 \pm 0.2$ ns, 4:1 acetonitrile:water) and suggests that CLH^+ adopts a more rigid geometry as a result of extensive hydrogen bonding.

The effect of concentration and added water on the transient absorption spectrum of CL are shown in Figure 4. Irradiation (355 nm) of an acetonitrile solution of CL generates both CL^* and CLH^{+*} species (Figure 2c). The transient absorption spectrum of CL in acetonitrile (Figure 4a) shows a broad absorption of low intensity centered at 525 nm which persists for more than 5 ns in the dilute solution. This absorbance is assigned to CLH^{+*} under conditions of low water concentration. When the concentration of CL is increased by a factor of 10 to 5×10^{-3} M (Figure 4b), this feature is reduced substantially and a new absorption appears at 460 nm after 5 ns. Self-quenching of CL occurs at this concentration, and it is possible that the absorption at 460 nm in Figure 4b may be due to a small amount of self-quenched ligand (i.e. CL^+, CL^-). In 4:1 acetonitrile:water (Figure 4c), a new band appears at 625 nm which is assigned to CLH^{+*} in an extensive hydrogen-bonding solvation network. The negative absorbance seen in Figure 4c is a result of the enhanced emission of CLH^{+*} at 486 nm which cancels out much of the absorption in this region.

Ligand Cation Radical Spectrum. Three quenchers MV^{2+} ($E°(2+/+) = -0.448$ V vs NHE),[40] *p*-benzoquinone ($E°(0/-) = -0.31$ vs NHE),[41] and $[Co(bpy)_3]^{3+}$ ($E°(3+/2+) = 0.36$ vs

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(32) Only one emission is observed with $\lambda_{max} = 416$ nm in *n*-hexane, $\lambda_{max} = 411$ nm in diethyl ether, $\lambda_{max} = 416$ nm in THF, and $\lambda_{max} = 413$ nm in ethyl acetate.

(33) Sabbatini, N.; Dellonte, S.; Bonazzi, A.; Ciano, M.; Balzani, V. *Inorg. Chem.* **1986**, *25*, 1738.

(34) Haga, M.; Dodsworth, E. S.; Eryavec, G.; Seymour, P.; Lever, A. P. B. *Inorg. Chem.* **1985**, *24*, 1901.

(35) Andrews, D. L. *Chem. Phys.* **1989**, *135*, 195.

(36) Solomon, E. I.; Penfield, K. W.; Wilcox, D. E. *Struct. Bond.* **1983**, *53*, 5.

(37) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings Publishing Co.: Menlo Park, CA, 1978.

(38) $k_{en.trans} = J\kappa \exp(-2R/L) = 2 \times 10^{-4}$ s^{-1}: Ehrenberg, M.; Cronvall, E.; Rigler, R. *FEBS Lett.* **1971**, *18*, 199. Leese, R. A.; Wehry, E. L. *Anal. Chem.* **1978**, *50*, 1193.

(39) Reported as +1.34 V vs SCE: Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Non-aqueous Systems*; Marcel Dekker: New York, 1970.

(40) Wardnan, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1637.

(41) Reported as –0.55 V vs SCE: Mussell, R. D.; Nocera, D. G. *J. Am. Chem. Soc.* **1988**, *110*, 2764.

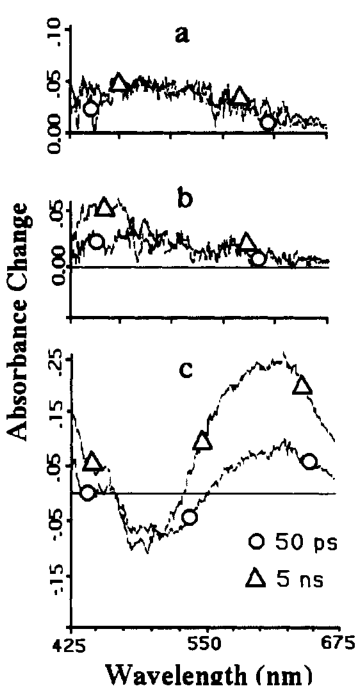

Figure 4. Picosecond transient absorption spectra of CL: (a) 5×10^{-4} M in acetonitrile, (b) 5×10^{-3} M in acetonitrile, and (c) 1×10^{-3} M in 5:1 acetonitrile:water.

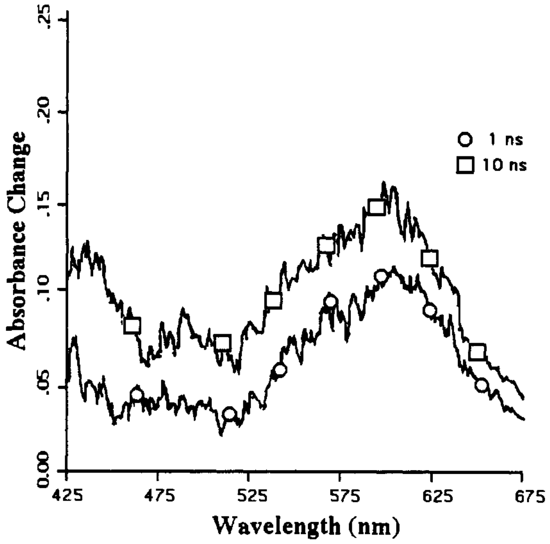

Figure 5. Picosecond transient absorption spectra of intermolecular quenching of the ligand excited state by methyl viologen dication. [CL] = 2.1×10^{-4} M, and [MV^{2+}] = 1.37×10^{-2} M in acetonitrile.

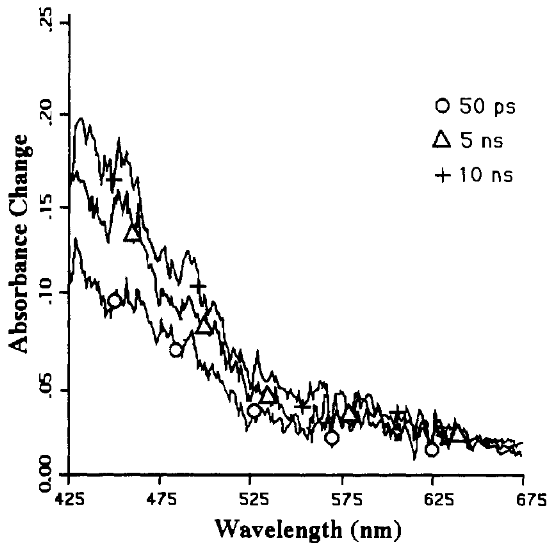

Figure 6. Picosecond transient absorption spectra of intermolecular quenching of the ligand excited state by *p*-benzoquinone. [CL] = 1.0×10^{-3} M, and [*p*-benzoquinone] = 0.10 M in acetonitrile.

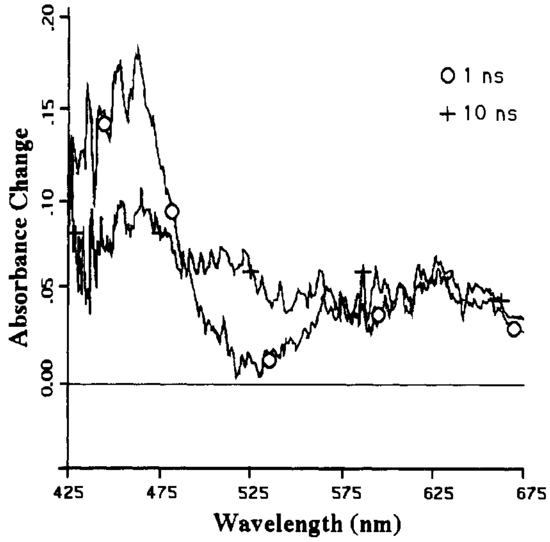

Figure 7. Picosecond transient absorption spectra of intermolecular quenching of the ligand excited state by [Co(bipyridyl)$_3$](ClO$_4$)$_3$. [CL] = 1.67×10^{-3} M, and [[Co(bipyridyl)$_3$](ClO$_4$)$_3$] = 4.1×10^{-2} M in acetonitrile.

NHE)[42] were used to generate the transient spectrum of CL$^+$, and the results are shown in Figures 5–7, respectively. To get these transient features, the concentration of quencher in acetonitrile had to be made large enough to cause efficient static quenching of CL*. In all cases, a single absorption band is seen at 480 nm (estimated ϵ = 6000 M^{-1} cm^{-1}) that we assign to the cation radical of CL. Thus, Figure 5 shows transient absorption spectra of intermolecular electron-transfer quenching of CL* by methyl viologen dication (MV^{2+}). The spectra show the transient absorption spectrum expected[43] for the reduced quencher, MV$^+$, with absorption maxima at 607 nm (ϵ = 13 900 M^{-1} cm^{-1})[44] and at 397 nm (ϵ = 41 800 M^{-1} cm^{-1}). The absorption at 440 nm in Figure 5 probably results from the low-energy shoulder of the very intense band at 397 nm. An additional band not associated with MV$^+$ appears at 480 nm which we assign to CL$^+$. A steady-state concentration of both species is established on the nanosecond time regime, and this appears as a growth in the entire spectrum from 1 to 10 ns. Similarly, Figure 6 shows the transient absorption spectra obtained at 50 ps, 5 ns, and 10 ns following the excitation pulse for the oxidative quenching of CL* by *p*-benzoquinone. The spectra consist of an absorption at 430 nm (ϵ = 7400 M^{-1} cm^{-1}) due to the *p*-benzoquinone anion radical which tails off toward the red, giving no absorption beyond 450 nm.[45] This leaves an additional absorption centered at 480 nm which can only be assigned to the CL cation radical. Figure 7 shows the transient absorption spectra resulting from oxidative quenching of CL* by [Co(bpy)$_3$]$^{3+}$. At 1 ns after the excitation pulse, only absorptions due to the ligand cation radical at 480 nm and the protonated excitated state at 625 nm are visible due to the lack of absorption of the reduced quencher, [Co(bpy)$_3$]$^{2+}$, in the visible region.[46] The absorption appearing at 510 nm in the spectrum

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[42] Determined in acetonitrile with 0.1 M TBAH electrolyte.

[43] Turk, T.; Resch, U.; Fox, M. A.; Vogler, A. *Inorg. Chem.* **1992**, *31*, 1854.

[44] Watanabe, T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617.

[45] Yoshimura, A.; Ohno, T. *Photochem. Photobiol.* **1991**, *53*, 175.

[46] (a) Schlafer, E. *Z. Phys. Chem.* **1956**, *8*, 373. (b) Martin, B.; Waind, G. M. *J. Chem. Soc.* **1958**, 4284.

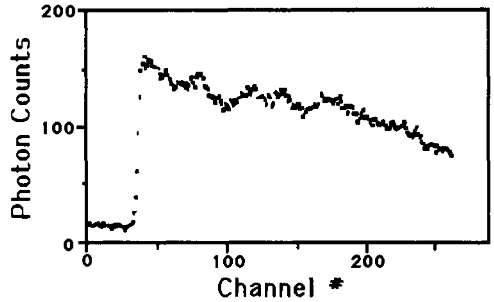

Figure 8. Emission decay data with a streak camera speed of 26.6 ps/channel of $Zn(CL)(H_2O)_2(ClO_4)_2$ at 4×10^{-4} M in acetonitrile.

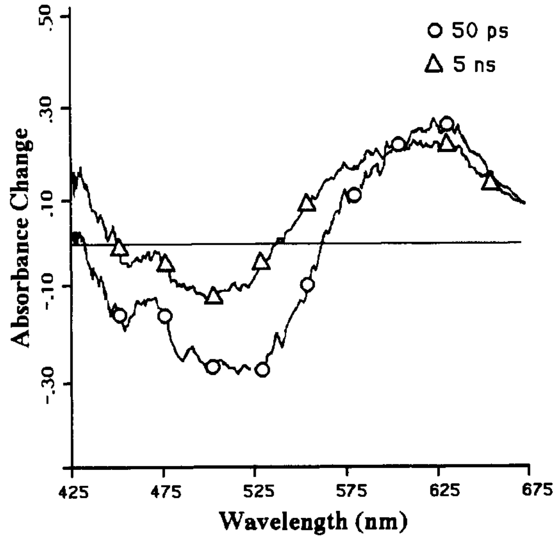

Figure 9. Picosecond transient absorption spectra of the zinc reference complex, $Zn(CL)(H_2O)_2(ClO_4)_2$, at 4×10^{-4} M in acetonitrile.

recorded after 10 ns may be due to a Co(II) substitution product or a CL^+ decomposition product.[47]

Intramolecular Electron Transfer. For the metal complexes, the chromophore ligand is mostly protonated in the ground state and when irradiated only emission from CLH^{+*} is observed (Figure 2d,e). The Zn(II) ion is not expected to quench the chromophore ligand, and the emission decay of **4** (Figure 8) was found to have a lifetime of 9.3 ± 0.3 ns. This is close to the lifetime of CLH^{+*} in 4:1 acetonitrile:water, and similarly the transient absorption spectrum of this complex (Figure 9) shows a significant absorbance centered at 625 nm at 50 ps and 5 ns following the excitation pulse. No evidence for the formation of the ligand cation radical was observed, and in fact the zinc complex displayed stimulated emission from the protonated excited state at 485 nm on the 50-ps time scale as determined by a comparison of the emission from the complex in the presence and absence of the probe pulse.

In the case of **1**, the driving force for electron transfer to form the Cu(I) species is estimated[48] to be 1.36 V. In Figure 10a, the emission decay of this complex displays a very fast component with a lifetime of 18 ± 1 ps and a much slower component with a lifetime of 3.14 ± 0.04 ns. Picosecond transient absorption spectra for **1** (Figure 11) display the rapid formation of the chromophore cation radical by the appearance of the absorption centered at 480 nm. The 480-nm absorption is of slightly larger intensity at 20 ps following excitation as it is when the 30-ps duration excitation and the probe continuum pulse are passed through the sample simultaneously, labeled 0 ps in Figure 11. This means that when the sample has been exposed to half of the excitation pulse or about 15 ps (i.e. 0-ps curve), most of the cation radical has been formed and all of the cation radical is formed within 5 ps after the excitation pulse ends (i.e. 20-ps curve). This gives a lifetime of formation (τ_f) for the cation radical of 15 ± 5 ps much in agreement with the 18 ± 1 ps component of the emission decay curve. The cation radical then decays (τ_b) with lifetime of 294 ± 8 ps presumably by back-electron-transfer to form the Cu(II) complex. Back-electron-transfer has a driving force[49] of 1.90 V which would be well into electron-transfer inverted region behavior by analogy with other systems.[1,2,9,50,51] The protonated excited-state absorbance at 625 nm decays with a lifetime of 4 ± 3 ns. There is a large uncertainty in this value

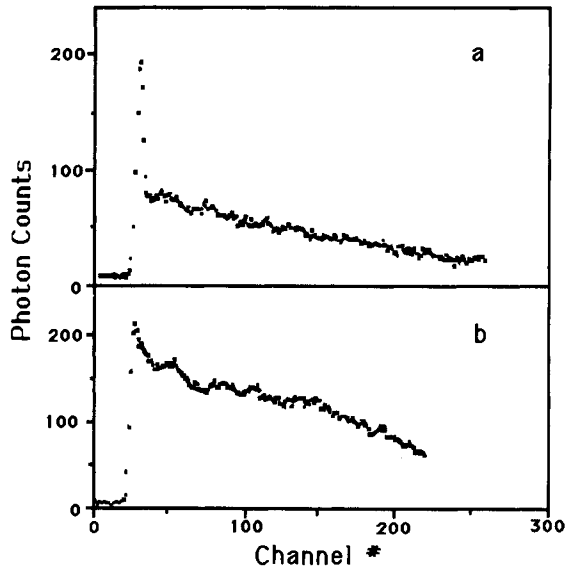

Figure 10. Emission decay data with a streak camera speed of 26.6 ps/channel of (a) $Cu(CL)(CF_3SO_3)_2$, 0.01 M in acetonitrile, and (b) $Cu(CL)(H_2O)_2(CF_3SO_3)_2$, 0.015 M in acetonitrile.

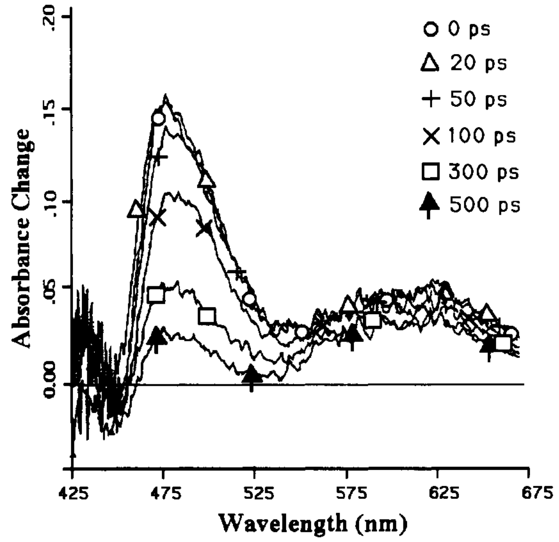

Figure 11. Picosecond transient absorption spectra of intramolecular quenching of the ligand excited state in $Cu(CL)(CF_3SO_3)_2$ at 1.15×10^{-3} M in acetonitrile.

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(47) The rapid decay of the cation radical absorption is not seen when the excited ligand is quenched by MV^{2+} or benzoquinone. When CL is placed together with $[Co(NH_3)_5(CF_3SO_3)]^{2+}$ in acetonitrile the complex $[Co(CL)_3]^{3+}$ forms. The suggested mechanism for this reaction is that Co(III) oxidatively quenches the excited state of CL. The resulting Co(II) complex is substitutionally labile and rapidly binds to CL^+. Electron transfer results in the re-formation of Co(III) and neutral CL. Further studies are in progress on this system.

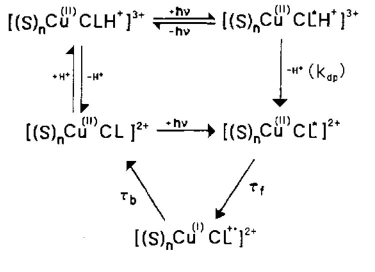
(48) $E_p(Cu^{II/I}) = -0.50$ V vs NHE; this gives $\Delta E° = 1.86 - 0.50 = +1.36$ V.

(49) $\Delta E° = E_{red}(CL^{+/0}) - E_{ox}(Cu^{+/2+}) = 1.40 + 0.50 = +1.90$ V.

(50) Carrol, F. A.; McCall, M. T.; Hammond, G. S. *J. Am. Chem. Soc.* **1973**, *95*, 315.

(51) Murtaza, Z.; Zipp, A. P.; Worl, L. A.; Graff, D.; Jones, W. E., Jr.; Bates, W. D.; Meyer, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 5113.

Scheme 1



due to the low extinction coefficient for this absorption coupled with the relatively high level of noise on the spectra in this region. By analogy with the chromophore ligand and the zinc complex, this absorption due to the protonated excited state would be expected to have a lifetime of the order of 7–11 ns. The shorter lifetime and the large difference in quantum yields of emission for complex **1** compared to **4** can be explained if competitive deprotonation (k_{dp}) occurs followed by rapid electron transfer to form cation radical CL$^+$ and Cu(I). The photophysical and photochemical processes initiated by excitation of the chromophore–quencher complexes are summarized in Scheme 1.

Transient absorption spectra were also recorded at higher concentrations of 0.05 M to rule out the possibility that the observed quenching and decay processes were influenced by intermolecular reactions. The formation and decay of the cation radical was unchanged by this, while the decay of the protonated excited state became more uncertain due to added spectral noise and thermal lensing effects. Transient absorption of the non-chromophore–quencher complex **3** displayed no observed transients in the 425–675-nm range, thus eliminating the possibility that the observed cation radical spectrum was due to a LMCT band. By analogy with a number of Cu(I) complexes with nitrogen ligands,[52] any MLCT bands due to the reduced metal would also be expected to be higher in energy than the observed 425-nm limit of the current spectra.

The emission decay of **2** (Figure 10b) is significantly different from that seen for **1** (Figure 10a). For **2** the fast decay component has $\tau = 21 \pm 1$ ps and is followed by a slow decay component with $\tau = 4.2 \pm 0.1$ ns. The transient absorption study of this complex (Figure 12) shows that the radical cation absorption at 480 nm reaches a maximum in less than 100 ps and decays with a lifetime of 360 ± 20 ps. A band centered at 625 nm due to CLH^{+*} also reaches a maximum in less than 100 ps but decays far more slowly with a lifetime of 5 ± 1 ns in good agreement with the emission decay ($\tau = 4.2 \pm 0.1$ ns) obtained from Figure 10b. It is important to note that the 625-nm absorption band in Figure 12 is more intense relative to the radical cation band at 480 nm than it is in Figure 11 for the anhydrous complex **1**. This is expected since the quantum yields for emission from CLH^{+*} reflect that CLH^{+*} is generated far more efficiently in complex **2** than **1** and this may be a consequence of water coordination in **2**. The acidity of coordinated water is expected to be enhanced, and this should facilitate the formation of a protonated excited state. On the other hand, complex **2** will convert to **1** if recrystallized from dry acetonitrile, and so the appearance of the radical cation absorption band in Figure 12 may have a significant contribution from an impurity of complex **1** in an acetonitrile solution of **2**. In any case, the formation of CLH^{+*} seems to deactivate the electron-transfer quenching of the chromophore–quencher complex.

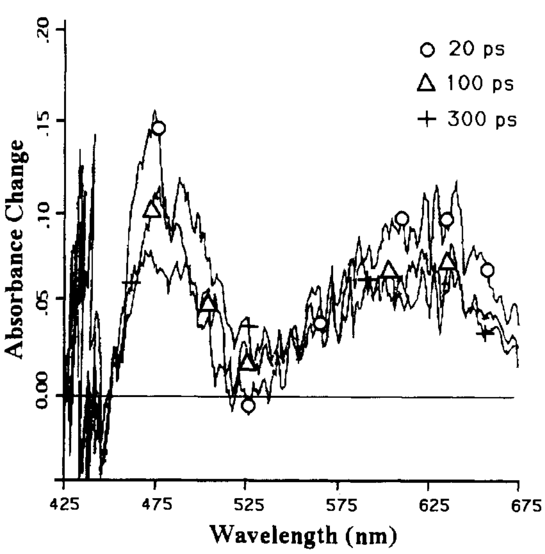


Figure 12. Picosecond transient absorption spectra of intramolecular quenching of the ligand excited state in Cu(CL)$(H_2O)_2(CF_3SO_3)_2$ at 1.0 × 10^{-3} M in acetonitrile.

Future Studies

We have shown that a charge-separated state having a lifetime of approximately 300 ps can be formed from oxidative quenching of an organic chromophore bound to a metal quencher. In order for a system of this type to be useful for photocatalytic applications, several conditions must be satisfied:[53] (i) Dissociation of the photoactive ligand does not occur. (ii) Both the excited state and the subsequent charge-separated state are not quenched by an energy-transfer mechanism. (iii) H$^+$ and H$^\bullet$ transfer on the ligands are slow compared to electron transfer. The system prepared for this study fulfills the first two requirements, but proton transfer to the chromophore excited state occurs much too rapidly in these complexes for charge separation to be efficient. This can be circumvented by working with neutral complexes that are soluble in truly "water-free" solvents. Another factor not considered above is that the lifetime of the charge-separated state is too short at 300 ps to carry out a bimolecular chemical reaction at the metal center. On this time scale, only intramolecular rearrangement is competitive with back-electron-transfer. To facilitate the formation of a long-lived charge-separated state, the back-electron-transfer rate must be reduced, and the most convenient method to delay this inverted region process would be to increase the thermodynamic driving force. This can be easily accomplished by dealkylating the *n*-butoxy moieties on the chromophore to form a hydroquinone-like chromophore. The resulting ligand would have a significantly higher excited-state redox potential (approximately −2.1 V) and in addition would function as a chemically reversible 2-electron reservoir for multielectron processes.

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