Phenylethynyl Substituent Effects on the Photophysics and Electrochemistry of [Cu(dpp)₂]⁺ (dpp = 2,9-Diphenyl-1,10-phenanthroline)

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The syntheses, absorption spectra, emission spectra, electrochemical behavior, and excited-state lifetimes of a series of phenylethynyl-substituted copper(I) complexes are reported. These results are compared to those of the parent complex, [Cu(dpp)₂]⁺ (dpp = 2,9-diphenyl-1,10-phenanthroline), to explore the effects of extended electronic delocalization on the photophysics of luminescent copper(I) bis(phenanthroline) complexes. Visible excitation of these complexes leads to emission from metal-to-ligand charge-transfer excited states. Room-temperature excited-state lifetimes range from 91 to 243 ns in dichloromethane. The effects of the phenylethynyl group(s) on the photophysical and electrochemical properties vary with the position of substitution. The most profound effects are observed when the parent complex is substituted at the 4- and 7-positions of the phenanthroline ligand. The positional effects are discussed with respect to the nature of the lowest unoccupied molecular orbitals.

Introduction

Although polypyridine complexes of ruthenium(II) receive a great deal of attention from groups researching photoinduced electron and energy transfer,[1-4] copper(I) polypyridine complexes also display interesting photoluminescent properties. In recent years, our group and other researchers[5-8] have been interested in examining the properties and applicability of copper(I) bis(phenanthroline) complexes. We recently reported a heteroleptic copper(I) complex, [Cu(dbp)(dmp)]⁺ (dbp = 2,9-di-*tert*-butyl-1,10-phenanthroline; dmp = 2,9-dimethyl-1,10-phenanthroline), which has solution-state properties that rival those of what is probably the most studied photoluminescent transition-metal complex, [Ru(bpy)₃]²⁺ (bpy = 2,2′-bipyridine).[9]

A major focus of our research is to develop the photochemistry of copper(I) bis(phenanthroline) complexes in order to make them suitable for practical applications such as light harvesting for photovoltaic cells and as molecular sensors. For a complex to be useful as a molecular sensor, the complex should have a high quantum yield of photoluminescence. Until recently, a major limitation in the use of copper(I) bis-(phenanthroline) complexes was their low quantum yields ($\phi \approx 0.001$).[8,10] With the discovery of the highly luminescent complex [Cu(dbp)(dmp)]⁺,[9] our focus has turned toward increasing the ability of copper bis(phenanthroline) complexes

to absorb in the visible region. We are also interested in exploring the effects of extended electronic delocalization in the metal-to-ligand charge-transfer (MLCT) acceptor ligands. It has been shown that increased π-delocalization in the acceptor ligands can have a dramatic effect on the photophysical properties of ruthenium(II) polypyridine complexes.[11-16] Lifetime enhancements (up to a factor of 3000) have been observed in certain systems. These effects are thought to be due to a reduction in the amount of nuclear displacement in the MLCT excited state of the complex. Extending the delocalization of the acceptor orbital allows the effect of the excited electron to be dispersed over more atoms, causing less excited-state structural distortion, which slows nonradiative decay.
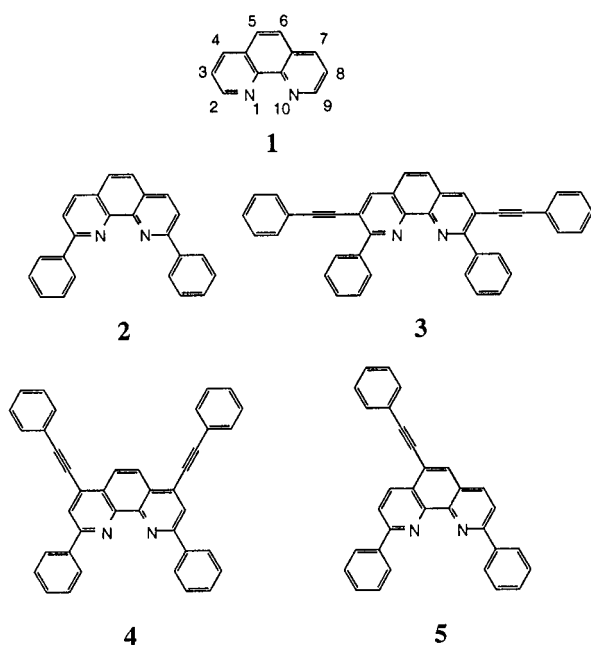
For light-harvesting applications, a device should absorb as much of the visible spectrum as possible to maximize the use of energy provided by the sun. All of the copper(I) complexes in this study are based upon the well-studied Cu^I complex of 2,9-diphenyl-1,10-phenanthroline, [Cu(**2**)₂]⁺ (Chart 1).[5-8,17-20] In the case of [Cu(**2**)₂]⁺, the complex absorbs over a wide region of the visible spectrum, from 400 to 650 nm with a maximum at 440 nm ($\epsilon = 3800$ M⁻¹ cm⁻¹). These absorption bands are

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Chart 1

Figure 1. Electronic absorption spectra of [Cu(**2**)₂]⁺, [Cu(**3**)₂]⁺, [Cu-(**4**)₂]⁺, and [Cu(**5**)₂]⁺, in dichloromethane at room temperature.

due to several MLCT transitions that generate [Cu^{II}(L)(L$^{\bullet-}$)]⁺ in the excited state.[21-24] Complex [Cu(**2**)₂]⁺ absorbs over a much broader region of the visible spectrum than [Cu(NN)₂]⁺ systems (NN = a 1,10-phenanthroline derivative) without phenyl substituents at the 2- and 9-positions of the phenanthroline ligand.[8] It is believed that the wider absorption manifold is due to a molecular fluxionality in the ground state which is likely stabilized by π-stacking interactions between the phenyl groups and the phenanthroline plane of the opposing ligand.[19,25] This fluxionality allows several transitions which are forbidden in an idealized D_{2d} symmetry to become allowed as the complex distorts to lower symmetry.[19,23,24,26,27] These interactions are clearly seen in the solid state.[25,28]

To shift the MLCT bands in [Cu(**2**)₂]⁺ further into the visible spectrum we focused on decreasing the energy of the LUMO by adding electron-withdrawing substituents to the phenanthroline. We selected the phenylethynyl group for our investigation since it should extend the delocalization regardless of the conformation of the phenyl group relative to the phenanthroline plane. The ethynyl group is also attractive from a synthetic point of view since it cannot form isomers, is chemically stable, and is easy to attach through known coupling methods.[29-32] Thus, we are able to examine the effects of phenylethynyl groups at different positions of the phenanthroline ligand (Chart 1).

The three goals of this study are (1) to increase the ability of [Cu(NN)₂]⁺ complexes to absorb visible light and thus, ideally, to make copper-based black absorbers, (2) to study the effects of extended delocalization of the photochemistry of [Cu(NN)₂]⁺ complexes, and (3) to study the effects of modifying the parent phenanthroline (**2**) at different positions. This paper describes the photophysical and electrochemical effects of substituting the parent complex, [Cu(**2**)₂]⁺, with phenylethynyl groups.

Experimental Section

Syntheses. Synthetic procedures used for the preparation of the ligands and the copper(I) complexes are provided in the Supporting Information.

Instrumentation. Electronic absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Luminescence spectra were recorded on a Perkin-Elmer LS-50B luminescence spectrometer equipped with a red-sensitive photomultiplier tube. Emission spectra were corrected using the files supplied by the instrument manufacturer. Time-resolved luminescence was studied using a pulsed dye laser pumped by a XeCl excimer laser. Details of these experiments have been previously provided.[33] Cyclic voltammograms were recorded on a BAS CV50W analyzer in a single cell with a glassy carbon working electrode, a Pt wire counter electrode, and a Ag/AgCl(aq) reference electrode. The Fc⁺/Fc couple was recorded at +0.450 V under identical conditions.

Results

(I) Electronic Absorption Spectra. The absorption spectra of the complexes are shown in Figure 1. All of the spectra show a common red shift in the ligand $\pi-\pi^*$ transition when the phenylethynyl group is attached to the parent ligand.[34-36] This red shift is taken as evidence of the extended electronic delocalization in the phenylethynyl-modified phenanthroline ligands. The MLCT transitions in the Cu^I complexes are also affected by the extended delocalization with ligands **3** and **4**, but not with ligand **5** (Figure 1).

The primary MLCT band of ruthenium(II) tris(diimine) complexes is known to be relatively insensitive toward substitution on the diimine ligands.[34] However, the phenylethynyl-substituted phenanthroline Ru^{II} complexes[34] are sensitive, and this is also the case with our Cu^I complexes. The copper complex of **4** shows a 1890 cm⁻¹ shift in the MLCT band compared to the parent complex [Cu(**2**)₂]⁺. The intensity of the

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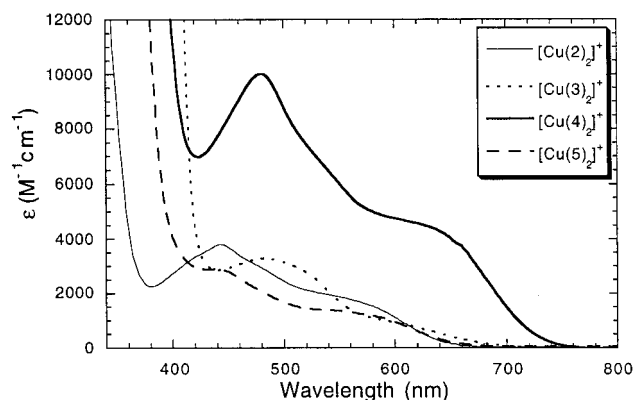(32) Grosshenny, V.; Romero, F. M.; Ziessel, R.; Suffert, J. *J. Org. Chem.* **1997**, *62*, 1491−1500.

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Table 1. Room-Temperature Photophysical and Electrochemical Data[a]

compd	λ_{max}abs, nm (ϵ)[b]	λ_{max}em, nm[c]	τ, ns[d]	$E_{1/2}[Cu(L)_2]^{2+/+}$	$E_{1/2}[Cu(L)_2]^{+/0}$	$E_{1/2}[Cu(L)_2]^{0/-}$
[Cu(**2**)$_2$](PF$_6$)	440 (3800)	690	243	0.84 (70)	−1.80[e]	i
[Cu(**3**)$_2$](PF$_6$)	482 (3300)	758	91	1.00 (66)	−1.35 (72)	−1.58 (66)
[Cu(**4**)$_2$](PF$_6$)	480 (10000)	773	108	0.89 (76)	−1.35 (66)	i
[Cu(**5**)$_2$](PF$_6$)	438 (2900)	740	238	0.88 (81)	−1.58[e]	i

[a] Redox couples were measured in a nitrogen-saturated dichloromethane solution containing 0.1 M TBAH at room temperature at 300 mV/s. Couples are reported in volts vs Ag/AgCl. The difference between the anodic and cathodic current peak potentials (in millivolts) is given in parentheses. [b] The molar extinction coefficient at the absorption maximum (M^{-1} cm^{-1}) is given in parentheses. [c] From corrected photoluminescence spectra ±5 nm (see text for details). [d] Excited-state lifetime in deoxygenated dichloromethane (±5%) with excitation at 535 nm. [e] Peak potential of a quasi-reversible process. i = irreversible.

primary MLCT transition also increases from 3800 M^{-1} cm^{-1} for [Cu(**2**)$_2$]$^+$ to 10 000 M^{-1} cm^{-1} for [Cu(**4**)$_2$]$^+$. As can be seen in Figure 1, the strong absorption throughout the visible region for [Cu(**4**)$_2$]$^+$ demonstrates that the complex is a black absorber. The MLCT band shapes, however, are largely unaffected by the phenylethynyl groups on the 4- and 7-positions of the phenanthroline.

The primary MLCT band of the copper(I) complex of **3** also shows a substantial red shift of 1980 cm^{-1} versus the parent complex, [Cu(**2**)$_2$]$^+$ (Figure 1). The intensity of the MLCT band is slightly decreased, and this effect has been seen in the Ru(II) complex of 3,8-diphenylethynyl-1,10-phenanthroline.[34] Careful inspection also shows that the low-energy shoulder of [Cu(**3**)$_2$]$^+$ is decreased in intensity relative to [Cu(**2**)$_2$]$^+$. This is expected since inspection of molecular models indicates that steric interactions between the phenylethynyl groups and the phenyl groups at the 2- and 9-positions will restrict the rotation of the phenyl groups. This, in turn, will reduce ground-state and excited-state distortions by enforcing D_{2d} symmetry in the complex and decrease the intensity of the low-energy shoulder.[19,26,28,33]

The visible electronic absorption spectrum of [Cu(**5**)$_2$]$^+$ is largely unaffected by the phenylethynyl substitution (Figure 1). There is a red shift in the ligand π−π* band, but there is no corresponding MLCT shift. As with [Cu(**3**)$_2$]$^+$, there is a slight decrease in the intensity of the MLCT bands.

(II) Electrochemical Properties. The cyclic voltammograms of the complexes were recorded in dichloromethane (Table 1). All of the complexes display a reversible Cu$^{II/I}$ redox couple. The Cu$^{II/I}$ couple is greatly influenced by the steric bulk of the substituents at the 2- and 9-positions of the phenanthroline ligands.[10,37] As these substituents become more bulky, the complex is unable to rearrange to the preferred (square-planar) copper(II) coordination geometry due to steric clashes with the opposing ligand. This stabilizes the Cu^I state and results in a more positive Cu$^{II/I}$ redox potential. Although the 2- and 9-substituents are not varied in this study, the effect can still be observed with [Cu(**3**)$_2$]$^+$. Whereas the potentials of the complexes with ligands **2**, **4**, and **5** are within 50 mV of one another, the Cu$^{II/I}$ couple for [Cu(**3**)$_2$]$^+$ occurs ca. 110 mV more positive than that for the other complexes. This is attributed to the phenylethynyl groups limiting the rotation of the phenyl groups at the 2- and 9-positions of the phenanthroline due to steric interactions. This hindered rotation then prevents the flattening distortion (toward square-planar) preferred by the Cu^{2+} ion.

All of the complexes display at least one quasi-reversible reduction process in dichloromethane (Table 1). The one-electron reduction is assigned to a ligand-based process to form [Cu^I(L)(L$^{•-}$)]^0.[10] As expected, the values of these reduction

potentials correlate with the number of electron-withdrawing phenylethynyl groups in the complex. Interestingly the [Cu(**3**)$_2$]$^+$ complex also displays a second reversible reduction process in dichloromethane at −1.58 V.

(III) Photophysical Properties. Photoluminescence was observed from each of the complexes upon excitation of the MLCT band. The room-temperature excited-state lifetimes and emission spectra were recorded in nitrogen-saturated dichloromethane (Table 1). The emission spectra of [Cu(**3**)$_2$]$^+$, [Cu(**4**)$_2$]$^+$, and [Cu(**5**)$_2$]$^+$ are too weak at room temperature and the instrument corrections too severe to allow reasonable determinations of absolute quantum yields. The excited-state lifetimes of the complexes decrease in the order [Cu(**2**)$_2$]$^+$ > [Cu(**5**)$_2$]$^+$ > [Cu(**4**)$_2$]$^+$ > [Cu(**3**)$_2$]$^+$. Assuming that the excited-state distortion at the copper center is roughly equal for the complexes, the energy-gap law states that the value of the nonradiative decay rate constant is inversely related to the energy gap between the ground and excited states.[14−16,38] This effect has been previously observed in Ru^{II} tris(diimine) black absorbers.[39] Since the complexes in this study have the same core structure, the excited-state lifetimes can be expected to decrease with decreasing emission energy. The complexes can be listed in order of decreasing emission energy as follows: [Cu(**2**)$_2$]$^+$ > [Cu(**5**)$_2$]$^+$ > [Cu(**3**)$_2$]$^+$ > [Cu(**4**)$_2$]$^+$. This trend is very similar to the observed trend in excited-state lifetimes; however, the last two entries are reversed. The emission maxima of [Cu(**3**)$_2$]$^+$ and [Cu(**4**)$_2$]$^+$ are, however, quite close in energy, and the lifetimes are also reasonably close (Table 1). Thus, the energy-gap law holds reasonably well in correlating the excited-state lifetimes with the emission maxima in this series of complexes.

Discussion and Conclusions

We have prepared three new phenanthroline-based ligands with extended π-delocalization. If the areas under the absorption spectra (from 14 300 to 25 000 cm^{-1}) are integrated, the new ligands enhance the ability of the copper(I) complexes to absorb visible light in the order [Cu(**4**)$_2$]$^+$ > [Cu(**3**)$_2$]$^+$ > [Cu(**5**)$_2$]$^+$. It is shown that substituting the phenanthroline at the 4- and 7-positions with phenylethynyl groups has the most profound effect on the absorption spectrum and the emission energy of the resulting complex.

These substituent effects can be explained by examining the LUMO diagrams of 1,10-phenanthroline (Figure 2).[40] It has been shown that there are two low-lying MOs, a$_2(\chi)$ and b$_1(\psi)$, which are both possible acceptor orbitals in the MLCT excited state.[27,41]

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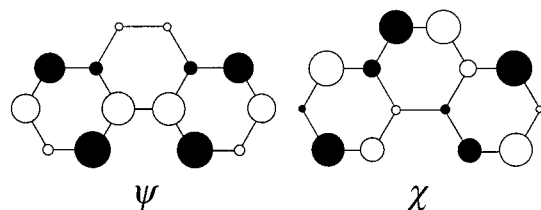
Figure 2. Schematic representation of the relative weights of the constituent pπ atomic orbitals for the two low-lying LUMOs of 1,10-phenanthroline.

Due to larger overlap between the metal d orbitals and the b$_1(\psi)$ orbital, it is generally agreed that MLCT excitation leads to population of the b$_1(\psi)$ orbital in these complexes.[27,41] Assuming that the MO coefficients do not change significantly due to phenyl substitution at the 2- and 9-positions, it is clear that in the b$_1(\psi)$ orbital there are large differences between the coefficients at the 3/8-, 4/7-, and 5/6-positions. The largest electronic effects should be observed for 4/7- and 3/8-substitution, whereas substitution at 5/6 should have a small or negligible effect (Figure 2). These predictions are confirmed by our experimental results that show significantly red-shifted MLCT bands for [Cu(**3**)$_2$]$^+$ and [Cu(**4**)$_2$]$^+$, but not for [Cu(**5**)$_2$]$^+$ (Figure 1). The MLCT intensities for [Cu(**3**)$_2$]$^+$ and [Cu(**4**)$_2$]$^+$, however, vary significantly. The enhanced absorption in [Cu(**4**)$_2$]$^+$ may be due to an increase in the dipole length of the transition that results from the geometric position of the phenylethynyl substituents.[27]

Upon phenylethynyl substitution, the photophysical properties of the parent complex, [Cu(**2**)$_2$]$^+$, are affected in a negative fashion in terms of excited-state lifetimes and quantum yields. It was hoped that the increased delocalization would enhance the ability of the complexes to absorb in the visible region while also enhancing the excited-state lifetimes of the complexes by reducing the nonradiative rate constant, as observed in certain

Ru^{II} systems.[11–16] As pointed out by Treadway et al., however, spectral fitting and temperature-dependent lifetime measurements are required to specifically determine the causal relationship between ligand delocalization and lifetime values.[15] From our results, it appears that, to take advantage of the broad absorption spectrum of the Cu^I complexes, one needs to use a relatively nonrigid complex that can distort away from D_{2d} symmetry. This is the exact opposite of what is required for a long excited-state lifetime and high quantum yield in a [Cu(NN)$_2$]$^+$ system.[9]

All of the novel complexes prepared here do have lifetimes which are long enough for bimolecular energy or electron transfer to occur. In addition, the ability of [Cu(**4**)$_2$]$^+$ to harvest solar energy is a marked improvement over the parent complex, [Cu(**2**)$_2$]$^+$, which has been previously used in a scheme to produce hydrogen gas from water and to sensitize large band gap semiconductors.[42–44] Thus, the utilization of [Cu(**4**)$_2$]$^+$ in place of [Cu(**2**)$_2$]$^+$ would be expected to lead to improved efficiencies in these two applications.

Supporting Information Available: Full synthetic procedures for the ligands **3**, **4**, and **5** and the copper(I) complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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