Photoinduced Electron Transfer and Electronic Energy Transfer in Naphthyl-Appended Cyclams

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A series of novel macrocyclic tetraaza ligands that incorporate a naphthalene moiety as a photoactive chromophore have been prepared and structurally characterized as their Cu(II) complexes. Variable-temperature photophysical studies have concluded that the luminescence quenching evident in the Cu(II) complexes is due to intramolecular electronic energy transfer (EET). In their free-base forms, these ligands undergo reductive luminescence quenching via photoinduced electron transfer (PET) reactions, with proximate amine lone pairs acting as electron donors. Consequently, the emission behavior can be modulated by variations in pH and/or the presence of other Lewis acids such as Zn(II).

Introduction

The excited state of a photoactive chromophore can be influenced by a variety of photophysical reactions. In the absence of other pathways, nonradiative relaxation via vibronic coupling or radiative relaxation via luminescence occurs. However, if the chromophore is in proximity to another molecule, interaction can lead to additional relaxation pathways such as photoinduced electron transfer (PET) or electronic energy transfer (EET). These two processes are quite well understood, and they form the basis of the fluorescent signaling used in a variety of supramolecular devices.[1−3]

Such devices usually incorporate three components whereby a fluorescent molecule is tethered to a binding unit appropriate for the analyte in question via a suitable linker; the presence or absence of the analyte is reported by a change in the fluorescent properties of the system. These devices have evolved for a variety of applications ranging from the detection of trace metal ions and other chemical analytes such as SO_4^{2-}, CO_2, and H_3O^+ to the measurement of physical properties such as temperature.[4−8]

A number of ligands that incorporate 1,4,8,11-tetraazacyclotetradecane (cyclam) as the binding unit have appeared in the literature bearing pendant fluorescent groups such as naphthalene or anthracene.[9−11] However, the vast majority of these involve the incorporation of fluorescent groups via covalent attachment to the macrocyclic nitrogen donor atoms[9−11] or through some modification to the cyclam framework.[12] This can lead to significant differences in both the binding ability of the ligand and the redox potentials of a bound metal ion. Therefore, the focus of our work involves the incorporation of fluorescent groups in such a way as to leave the cyclam core relatively unchanged.

Recently, we reported a macrocyclic ligand with a pendant anthracene group.[13] Here, we have extended this work and report our most recent results in the form of the preparation and characterization of a series of macrocylic ligands that incorporate the naphthalene moiety bound to cyclam via an amino pendant arm. As the distance between a photoactive component and a quencher can play an important role in the observed quenching mechanism, the effect of intercomponent separation was also investigated. This was facilitated by the use of the 1- and 2-naphthaldehyde isomers to induce structural variations in these systems.

Experimental Section

Safety Note. All preparative work was carried out in the fume hood. Perchlorate salts are potentially explosive. Although no problems were encountered, perchlorate salts should be handled only in small quantities and should never be scraped from sintered glass frits or heated in the solid state.

Syntheses. The parent macrocycle, *trans*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine hexahydrochloride, **L^1**·6HCl, was prepared according to previously reported methods.[14] Unless otherwise stated, all other reagents were obtained commercially and used as supplied without further purification.

***trans*-6-(1-Naphthalenylmethylamino)-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecan-13-amine, L^2. L^1·**6HCl (5.08 g, 10.6 mmol) was suspended in an EtOH/H_2O mixture (3:1 v/v, 200 mL), and NaOH (1 M) was added to dissolve the ligand. The pH of the resulting clear solution was adjusted to ca. 5.5 with NaOH (1 M), and Na[CN(BH_3)] (1.35 g, 21.5 mmol) was added. The pH was then readjusted to 5.5 with NaOH (1 M) prior to the addition of 1-naphthaldehyde (1.68 g, 10.7 mmol), and the resulting solution was stirred at room temperature

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for ca. 1 h while the pH was maintained at ca. 5.5 by the addition of aliquots of HCl (1 M) as required. After the reaction, EtOH was removed at reduced pressure and the pH was adjusted to greater than 12.0 with NaOH (5 M). The solution was extracted three times with $CHCl_3$ (75 mL), and the organic layers were collected and dried over anhydrous Na_2SO_4. The removal of $CHCl_3$ at reduced pressure gave the desired product as a yellow oil (ca. 3.2 g). Further purification, as the Cu(II) complex, was performed by cation exchange chromatography as described below.

[(*trans*-6-(1-Naphthalenylmethylamino)-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecan-13-amine)copper(II)] Perchlorate, [Cu(L^2)]-(ClO_4)$_2$. The crude free ligand $\mathbf{L^2}$ (ca. 3.2 g) was dissolved in an EtOH/H_2O mixture (1:1 v/v, 100 mL), and excess $Cu(OAc)_2 \cdot H_2O$ was added giving an immediate purple solution. EtOH was removed at reduced pressure leaving a suspension that persisted after gravity filtration. The water-insoluble organic byproducts, identified to be mostly 1-naphthalenemethanol by ^{1}H NMR, were removed by washing the aqueous solution (acidified to pH 4−5) with $CHCl_3$ (75 mL). This yielded a purple aqueous layer that was neutralized and sorbed onto a Sephadex C-25 cation exchange column (Na^+ form). Initially, the eluent was NaOAc (0.2 M), which gave three bands. Aqueous copper(II) eluted first as a green band and then traces of unreacted $[Cu(\mathbf{L^1})]^{2+}$. The desired product eluted last as a purple band after increasing the eluent concentration to 0.5 M. Addition of excess $NaClO_4$ to this band gave the immediate and quantitative precipitation of the desired product as a light-purple solid with cocrystallized NaOAc present as an impurity. The desired product was recrystallized by dissolving in CH_3CN, followed by gravity filtration to remove the NaOAc. Vapor diffusion of $(CH_3CH_2)_2O$ into the filtrate afforded X-ray quality crystals (0.45 g, 8%). Further crops of the complex could be obtained from the filtrate.

Electronic spectrum (CH_3CN): λ_{max} (ϵ) = 500 nm (79 M^{-1} cm^{-1}), 281 (9540), 271 (10 100), 223 (72 500). Elemental analysis, found: C, 42.05%; H, 6.01%; N, 13.22%. Calcd for $C_{23}H_{36}N_6Cl_2O_8$: C, 41.79%; H, 5.79%; N, 12.72%.

***trans*-6-(2-Naphthalenylmethylamino)-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecan-13-amine, L^3.** $\mathbf{L^3}$ was prepared in a manner similar to that used for $\mathbf{L^2}$, using 2-naphthaldehyde.

[(*trans*-6-(2-Naphthalenylmethylamino)-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecan-13-amine)copper(II)] Perchlorate Hydrate, [Cu(L^3)](ClO_4)$_2 \cdot H_2O$. As for $[Cu(\mathbf{L^2})]^{2+}$, the crude free ligand, $\mathbf{L^3}$, was purified as its Cu(II) complex. The NaOAc eluent concentration was increased to 2 M to remove the desired product from the chromatography column. Addition of $NaClO_4$ to this band gave the immediate and quantitative precipitation of the desired product as a pink powder with NaOAc as a cocrystallized impurity. This was purified, and X-ray quality crystals of $[Cu(\mathbf{L^3})](ClO_4)_2 \cdot H_2O$ were obtained in the manner described for $[Cu(\mathbf{L^2})](ClO_4)_2$.

Electronic spectrum (CH_3CN): λ_{max} (ϵ) = 502 nm (61 M^{-1} cm^{-1}), 264 (8150), 258 (7980), 223 (67 400). Elemental analysis, found: C, 40.51%; H, 5.77%; N, 11.85%. Calcd for $C_{23}H_{36}N_6Cl_2O_8$: C, 40.68%; H, 5.94%; N, 12.38%.

***trans*-6,13-Dimethyl-15-naphthalen-2-yl-1,4,8,11,14-pentaazabicyclo-[11.2.1]hexadec-6-ylamine, L^4.** $\mathbf{L^1} \cdot 6HCl$ (10.14 g, 21 mmol) was suspended in an EtOH/H_2O mixture (1:1 v/v, 200 mL), and NaOH (1 M) was added to dissolve the ligand. The pH of the solution was adjusted to 6.4 with NaOH (1 M). A sample of 2-naphthaldehyde (3.34 g, 21 mmol) was then added, and the resulting solution was refluxed for ca. 16 h, during which time a yellow color developed. Excess EtOH was removed at reduced pressure; the pH of the resulting solution was adjusted to greater than 12.0 with NaOH (5 M), and then the solution was extracted three times with $CHCl_3$ (75 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. Removal of the solvent at reduced pressure gave the desired product as a yellow oil (ca. 6.4 g), which was further purified, as the Cu(II) complex, by cation exchange chromatography.

[(*trans*-6,13-Dimethyl-15-naphthalen-2-yl-1,4,8,11,14-pentaazabicyclo[11.2.1]hexadec-6-ylamine)copper(II)] Perchlorate, [Cu-(L^4)](ClO_4)$_2$. The crude free ligand $\mathbf{L^4}$ (ca. 6.4 g) was dissolved in an EtOH/H_2O mixture (1:1 v/v, 100 mL), and excess $Cu(OAc)_2 \cdot H_2O$ was added giving an immediate purple solution. The EtOH was removed at reduced pressure, and the remaining solution was gravity filtered prior to sorbing onto a Sephadex C-25 cation exchange column (Na^+ form). The column was eluted initially using NaOAc (0.2 M), which gave three major bands. The first was identified as aqueous copper(II), and the second was unreacted $[Cu(\mathbf{L^1})]^{2+}$. The desired product eluted as a slow-moving, intensely purple band. Addition of excess $NaClO_4$ and a reduction in volume (ca. 50 mL) gave a solid microcrystalline product upon prolonged standing, which was collected by vacuum filtration (0.43 g, 4%). Further crops of the complex could be obtained from the filtrate. X-ray quality crystals were grown by the vapor diffusion of $(CH_3CH_2)_2O$ into a concentrated solution of this solid in CH_3CN.

Electronic spectrum (CH_3CN): λ_{max} (ϵ) = 520 nm (155 M^{-1} cm^{-1}), 269 (8760), 254 (8320), 225 (74 900). Elemental analysis, found: C, 40.70%; H, 5.60%; N, 12.26%. Calcd for $C_{23}H_{36}N_6CuCl_2O_8 \cdot H_2O$: C, 40.81%; H, 5.66%; N, 12.42%. A slow-moving, minor fourth band was also observed but was not characterized.

Preparation of Metal-Free Ligands, L^2, L^3, and L^4. After cation exchange chromatography as their Cu(II) complexes, the purified free ligands of $\mathbf{L^2}$, $\mathbf{L^3}$, and $\mathbf{L^4}$ were obtained by the addition of excess $Na_2S \cdot 9H_2O$, which gave a precipitate of CuS after 10−15 min of stirring at room temperature. This was removed by gravity filtration, and the resulting solution was extracted three times with $CHCl_3$. The organic layers were combined and dried over anhydrous Na_2SO_4 yielding solutions of the pure free bases as confirmed by ^{1}H and ^{13}C NMR.

NMR Data. L^2: ^{1}H ($CDCl_3$) δ 1.04 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 2.10 (s br, 7H, NH), 2.5−2.8 (m, 16H, CH_2), 4.15 (s, 2H, CH_2NH), 7.3−7.5 (m, 4H, Ar), 7.7−7.8 (m, 2H, Ar), 8.2−8.3 (m, 1H, Ar); ^{13}C ($CDCl_3$) δ 22.9, 27.4, 43.8, 48.6, 48.7, 51.3, 55.4, 57.8, 60.7, 124.0, 125.47, 125.50, 125.8, 126.4, 127.6, 128.6, 131.9, 133.8, 136.8.

L^3: ^{1}H ($CDCl_3$) δ 1.05 (s, 3H, CH_3), 1.13 (s, 3H, CH_3), 1.96 (s br, 7H, NH), 2.3−2.8 (m, 16H, CH_2), 3.87 (s, 2H, CH_2NH), 7.4−7.5 (m, 4H, Ar), 7.7−7.8 (m, 3H, Ar); ^{13}C ($CDCl_3$) δ 23.2, 27.3, 46.3, 48.68, 48.72, 51.3, 55.2, 57.8, 60.7, 125.4, 125.8, 126.3, 126.9, 127.5, 127.5, 127.8, 132.5, 133.4, 138.9.

L^4: ^{1}H ($CDCl_3$) δ 1.02 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.86 (s br, 5H, NH), 2.0−3.2 (m, 16H, $-CH_2$), 4.21 (s, 1H, CH), 7.37−7.43 (m, 2H, Ar), 7.71−7.76 (m, 4H, Ar), 7.92 (s, 1H, Ar); ^{13}C ($CDCl_3$) δ 27.3, 27.7, 47.9, 49.2, 49.3, 49.5, 51.5, 59.8, 60.0, 60.9, 61.8, 64.2, 84.7, 125.3, 125.91, 125.94, 127.6, 127.8, 127.9, 128.2, 133.1, 133.7, 137.3.

Physical Methods. Electronic spectra were measured on a Perkin-Elmer Lambda 40 spectrophotometer using quartz cells. Emission spectra were collected on a Perkin-Elmer LS-50B spectrophotometer using electronic absorption maxima as the excitation wavelengths for all compounds. A 290 nm cut-off filter was employed to avoid the detection of higher-order excitation light, and both excitation and emission monochromators used slit widths of 5 nm. Low-temperature (77 K) emission spectra were recorded in CH_3CN glasses utilizing front face excitation to allow a qualitative comparison with room-temperature spectra. Nuclear magnetic resonance spectra were measured at 200 (^{1}H) and 50.3 MHz (^{13}C) on a Bruker AC200 spectrometer using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as a reference. Electrochemical measurements were performed with a BAS100B/W potentiostat using a glassy carbon working, platinum Pt auxiliary, and Ag/Ag^+ nonaqueous reference electrodes. Solutions contained ca. 5 mM analyte and 0.1 M Et_4NClO_4 in CH_3CN as the supporting electrolyte, and were purged with N_2 prior to measurements. Measured potentials were referenced to the ferrocene−ferrocenium couple. Aqueous pulse radiolysis experiments were performed with a 20 MeV linear accelerator at the ARPANSA Laboratories, Melbourne, as previously described.[13] Reductions were effected by radiolytically generated aquated electrons (e_{aq}^-) in the presence of deoxygenated aqueous 0.1 M *t*-BuOH. Oxidations were achieved with the $^{\bullet}OH$ radical by saturating each solution with N_2O prior to measurement.

Crystallography. Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections measured on an Enraf-Nonius CAD4 four-circle diffractometer employing graphite-monochromated Mo Kα radiation (0.71073 Å) and operating in the $\omega-2\theta$ scan mode. Data reduction and empirical absorption corrections (Ψ-scans) were performed with the WINGX[15] package. Structures were

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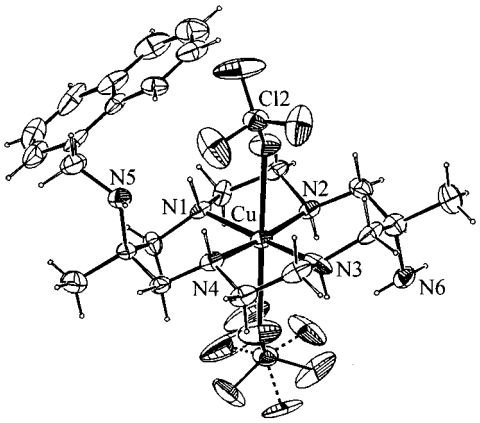


Figure 1. View of $[Cu(\mathbf{L^2})](ClO_4)_2$ (30% probability ellipsoids shown).

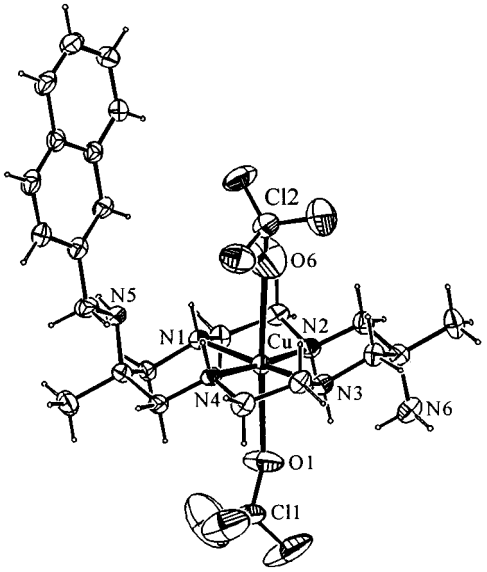


Figure 2. View of $[Cu(\mathbf{L^3})](ClO_4)_2 \cdot H_2O$ (30% probability ellipsoids shown). Solvent water omitted.

solved by the heavy atoms method with SHELXS-86[16] and refined by a full-matrix least-squares analysis with SHELXL-97.[17] For $[Cu(\mathbf{L^2})(CH_3CN)](ClO_4)_2 \cdot CH_3CN$, the crystal decomposed after ca. 90% of the data (to $2\theta = 50°$) was collected. Hydrogen atoms of noncoordinated water molecules were not modeled. Drawings of molecules (Figures1−4) were produced with PLATON97.[18]

Results and Discussion

Synthesis and Structure. The reductive alkylation reactions reported herein proceeded regioselectively, showing no evidence for reaction at the secondary amines of the cyclam core. Two isomeric products, $\mathbf{L^2}$ and $\mathbf{L^3}$, which differ only in the position of the naphthalene attachment, were obtained and could be easily purified from nonligating byproducts through cation exchange chromatography as their Cu(II) complexes. The formation of unwanted disubstituted products was also minimized at the optimal reaction pH of 5.5. Under these conditions, a single pendant amine is free to react with the aromatic aldehyde while the other is unavailable due to protonation.[19]

A third product, $\mathbf{L^4}$, was obtained when the reaction between $\mathbf{L^1}$ and 2-naphthaldehyde was conducted at elevated pH in the absence of a reducing agent. This bicyclic imidazolidine ligand

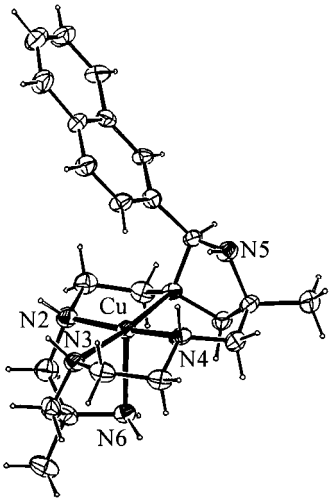


Figure 3. View of the $[Cu(\mathbf{L^4})]^{2+}$ complex cation (30% probability ellipsoids shown).

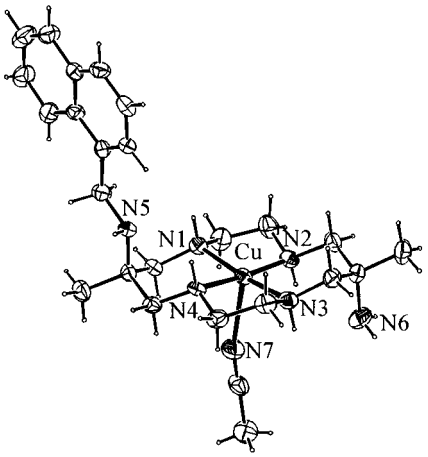
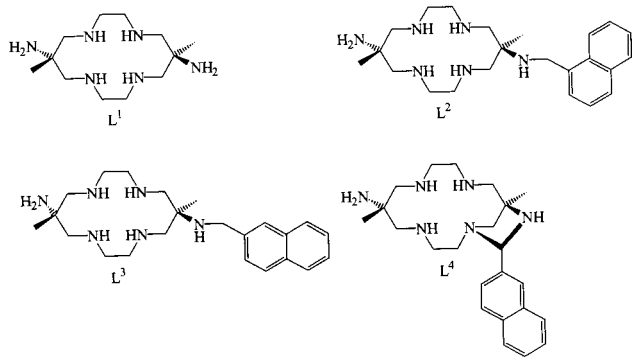


Figure 4. View of a polymorphic-solvated form of the $[Cu(\mathbf{L^2})]^{2+}$ complex cation (30% probability ellipsoids shown).

Chart 1



forms as a result of an intramolecular cyclization reaction involving the initial condensation imine intermediate and a secondary amine of the macrocyclic core. The 1-naphthaldehyde isomer did not display this behavior, most likely due to the increased steric crowding of the imine, which precludes nucleophilic attack. The Cu(II) complexes of these ligands were prepared and have been structurally characterized (Figures 1−4). The structures of $[Cu(\mathbf{L^2})](ClO_4)_2$ and $[Cu(\mathbf{L^3})](ClO_4)_2 \cdot H_2O$ were quite similar, both showing the complex cation on a general

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Table 1. Crystal Data

	$[Cu(\mathbf{L^2})](ClO_4)_2$	$[Cu(\mathbf{L^2})(CH_3CN)](ClO_4)_2\cdot(CH_3CN)$	$[Cu(\mathbf{L^3})](ClO_4)_2\cdot H_2O$	$[Cu(\mathbf{L^4})](ClO_4)_2$
empirical formula	$C_{23}H_{36}Cl_2CuN_6O_8$	$C_{27}H_{42}Cl_2CuN_8O_8$	$C_{23}H_{38}Cl_2CuN_6O_9$	$C_{23}H_{36}Cl_2CuN_6O_8$
formula weight, g/mol	661.03	743.09	677.03	659.02
crystal system	triclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
a, Å	8.4630(10)	8.185(3)	8.542(4)	9.324(2)
b, Å	9.1890(10)	34.853(7)	29.042(5)	13.3290(9)
c, Å	20.023(3)	12.178(6)	12.166(4)	23.3370(10)
α, deg	81.41(2)			
β, deg	88.10(2)	97.81(2)	106.60(2)	
γ, deg	66.950(10)			
V, Å^3	1416.2(3)	3442(2)	2892.3(17)	2900.2(7)
Z	2	4	4	4
T, K	293(2)	293(2)	293(2)	293(2)
λ, Å	0.71073	0.71073	0.71073	0.71073
μ, cm^{-1}	10.17	8.41	9.93	9.93
ρ_{calcd}, g/cm	1.550	1.307	1.509	1.509
$R(F_o)^a$	0.0738	0.0689	0.0482	0.0482
$wR2(F_o^2)^b$	0.1628	0.1624	0.1198	0.1198

^{a} $R(F_o) = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ ^{b} $wR2(F_o^2) = (\Sigma w(F_o^2 - F_c^2)/\Sigma wF_o^2)^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg)

	$[Cu(\mathbf{L^2})](ClO_4)_2$	$[Cu(\mathbf{L^2})(CH_3CN)](ClO_4)_2\cdot(CH_3CN)$	$[Cu(\mathbf{L^3})](ClO_4)_2\cdot H_2O$	$[Cu(\mathbf{L^4})](ClO_4)_2$
Cu−N1	2.008(8)	1.989(7)	2.002(5)	2.021(6)
Cu−N2	2.018(9)	1.996(7)	2.002(5)	2.010(6)
Cu−N3	1.929(10)	2.004(8)	2.013(5)	2.028(6)
Cu−N4	2.003(9)	1.997(7)	2.004(5)	2.008(6)
Cu−N6				2.307(6)
Cu−N7		2.476(10)		
Cu−naphthyl center	5.592	7.430	7.469	5.493
Cu−O1Cl1	2.509(9)		2.536(6)	
Cu−O5Cl2	2.604(7)		2.676(10)	
N1−Cu−N2	86.4(3)	86.4(3)	86.3(2)	86.2(3)
N1−Cu−N3	175.7(4)	172.4(3)	176.1(2)	173.7(3)

site. As with the known structures of $[Cu(cyclam)](ClO_4)_2$[20] and $[Cu(\mathbf{L^1})](ClO_4)_2$,[21] the perchlorate counteranions are bound axially perpendicular to the macrocyclic plane. The observed Cu−O and Cu−N bond lengths (see Table 2) are typical for complexes of this type. Both $[Cu(\mathbf{L^2})](ClO_4)_2$ and $[Cu(\mathbf{L^3})](ClO_4)_2\cdot H_2O$ display the common *trans*-III configuration of nitrogen donors first noted in cyclam due to the inherent stability associated with the alternating gauche and chair conformations of the five- and six-membered chelate rings, respectively.[22] In both structures, the pendant amine groups have adopted an axial (α) disposition with respect to the six-membered chelate rings to which they are bound. The major difference between these isomers is the position of the naphthalene fragment with respect to the macrocycle. In $[Cu(\mathbf{L^2})](ClO_4)_2$, the naphthalene points away from the macrocyclic plane with a separation between the metal and the center of the aromatic system of 5.592 Å. However, in $[Cu(\mathbf{L^3})](ClO_4)_2\cdot H_2O$, the naphthalene lies to one side of the macrocyclic plane with a separation of 7.469 Å. As evidenced by the structural similarity of $[Cu(\mathbf{L^2})](ClO_4)_2$ and $[Cu(\mathbf{L^3})](ClO_4)_2$ to $[Cu(cyclam)](ClO_4)_2$ and its amino-functionalized analogue, $[Cu(\mathbf{L^1})](ClO_4)_2$, our intention to introduce a fluorescent group by covalent modification while retaining an essentially unchanged cyclam core has been realized.

The crystal structure of $[Cu(\mathbf{L^4})](ClO_4)_2$ differed significantly as a result of the structural restraints imposed by the five-membered imidazolidine ring. The four equatorial donor nitrogens of the macrocycle have adopted the *trans*-I configuration, with the square pyramidal coordination sphere being completed by an axially coordinated pendant amino group with an elongated Cu−N bond length (Table 2). The naphthalene fragment is locked into position above the metal with a separation of 5.493 Å between the Cu atom and the center of the naphthyl group and effectively blocks the axial coordination site *trans* to the coordinated pendant amine. In this case, the perchlorate counteranions are not coordinated and the cyclam core has been altered by the introduction of a tertiary amine donor.

An unexpected but interesting polymorph of $[Cu(\mathbf{L^2})]^{2+}$ has also been structurally characterized, which contains two CH_3CN solvent molecules in the asymmetric unit. The crystal structure, shown in Figure 4, reveals that the macrocyclic ligand has adopted a configuration similar to that of the solvent-free structure shown in Figure 1. Both complexes have similar Cu−N bond lengths, display the *trans*-III configuration of nitrogen donors, and have an axial (α) disposition of pendant amines. However, the structures differ in that the solvated form is square pyramidal, with the fifth coordination site being occupied by a solvent CH_3CN, and the perchlorate counteranions are not coordinated. This has a dramatic bearing on the disposition of the naphthalene unit with respect to the macrocycle resulting in a significant change in the orientation and separation (∼2 Å) between the metal and the center of the aromatic system. Both crystals were grown by the vapor diffusion of $(CH_3CH_2)_2O$ into CH_3CN solutions of the complex, the only difference being the relative concentrations of the complex and the solvent.

The two forms of the $[Cu(\mathbf{L^2})]^{2+}$ complex serve to illustrate the conformational flexibility of the appended naphthyl group linkage in $[Cu(\mathbf{L^2})](ClO_4)_2$ and, presumably, $[Cu(\mathbf{L^3})](ClO_4)_2\cdot H_2O$. Similarly, they illustrate that in CH_3CN solution, axial ligands are most likely solvent molecules.

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Electrochemistry. Cyclic voltammetry of the Cu(II) complexes was measured in CH_3CN. Both $[Cu(\mathbf{L^2})]^{2+}$ and $[Cu(\mathbf{L^3})]^{2+}$ showed a reversible $Cu^{II/I}$ couple at ca. −1.465 V vs Fc/Fc^+ when the potential was reversed at −1.6 V. When the potential was swept below −1.6 V, an irreversible wave at −1.790 V was found and the $Cu^{II/I}$ couple also became irreversible. This behavior, consistent with that of the Cu(II) complexes of cyclam and other 14-membered tetraaza macrocycles,[23] is attributed to the electrochemical demetalation of the complex, and the more negative wave was assigned to the $Cu^{I/0}$ redox couple accordingly. This conclusion was supported by the appearance of a $Cu^{II/0}$ stripping wave at −0.77 V vs Fc/Fc^+ on the return oxidative sweep. For $[Cu(\mathbf{L^4})]^{2+}$, the $Cu^{II/I}$ redox couple was anodically shifted by ca. 0.3 V appearing at −1.134 V vs Fc/Fc^+. The significantly greater ease of reduction can be attributed to the longer Cu−N bond lengths of this complex, relative to those of $[Cu(\mathbf{L^2})]^{2+}$ and $[Cu(\mathbf{L^3})]^{2+}$, stabilizing the Cu(I) oxidation state.

The $[Cu(\mathbf{L^4})]^{2+}$ complex gave two distinct, irreversible redox couples in the oxidative sweep. The first, at +0.928 V vs Fc/Fc^+, was attributed to oxidations involving the amine lone pairs by comparison to the same oxidation in the parent, $[Cu(\mathbf{L^1})]^{2+}$, which appears at ca. +0.9 V vs Fc/Fc^+.[13] The second, appearing at +1.162 V vs Fc/Fc^+, has been assigned to the $Cu^{III/II}$ redox couple, which is anodically shifted compared to the same process in $[Cu(cyclam)]^{2+}$ (ca. +1.0 V vs Fc/Fc^+).[13,23] Oxidative sweeps of $[Cu(\mathbf{L^2})]^{2+}$ and $[Cu(\mathbf{L^3})]^{2+}$ gave overlapping, irreversible one-electron oxidation waves in the region from ca. 0.79 to 1.16 V vs Fc/Fc^+ from both amine lone pair oxidations and the $Cu^{II/III}$ redox couple. Resolution of these waves into their respective processes was not possible due to their occurrence at a similar potential.

Electronic Absorption Spectroscopy. The electronic spectra of $\mathbf{L^2}$, $\mathbf{L^3}$, $\mathbf{L^4}$, and their corresponding copper(II) complexes in CH_3CN are dominated by the intense absorption band at ca. 225 nm, which corresponds to the $S_0 \rightarrow S_3$ transition of the naphthalene chromophore.[24,25] At slightly lower energy, a broad band corresponding to the $S_0 \rightarrow S_2$ transition is also evident centered at ca. 270−280 nm. This band shows significant vibrational structure as a result of a Franck−Condon progression involving a naphthalene aromatic ring breathing mode. A third weak absorption is evident at ca. 310−320 nm and corresponds to the $S_0 \rightarrow S_1$ transition, which is only weakly electric dipole allowed.

In addition to these three bands, the copper(II) complexes also showed weaker metal-centered d−d transitions in the visible region at ca. 500 nm for $[Cu(\mathbf{L^2})]^{2+}$ and $[Cu(\mathbf{L^3})]^{2+}$ and at 520 nm for $[Cu(\mathbf{L^4})]^{2+}$. Molar extinction coefficients for the former two complexes were on the order of ca. 60−80 M^{-1} cm^{-1}, while the latter was significantly larger at ca. 160 M^{-1} cm^{-1} due to the decreased symmetry of the first coordination sphere. The position and intensity of these peaks are in general agreement with the values of the parent complex, $[Cu(\mathbf{L^1})]^{2+}$, and similar complexes in the same (α) N-based isomeric forms.[26,27]

Cu(II) complexes of tetraaza macrocycles such as cyclam and $\mathbf{L^1}$ also display intense, broad LMCT bands at ca. 250 nm.[28] Although not immediately apparent due to naphthalene absorption, this LMCT band was also present in the complexes of $\mathbf{L^2}$, $\mathbf{L^3}$, and $\mathbf{L^4}$, as evidenced by increases in the extinction coefficients for the metal complexes in the same 250 nm region compared to those of the free ligands. While this band has been known to lead to photoreactivity,[28] prolonged UV irradiation gave little evidence of d−d bleaching, indicating that photodecomposition of the complex was not taking place. This may in part be due to the strong naphthalene absorptions in this region insulating the LMCT band.

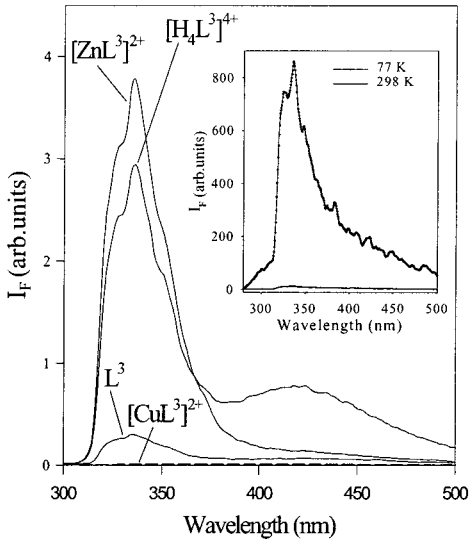

Figure 5. Fluorescence spectra of various $\mathbf{L^3}$ adducts in CH_3CN. Inset: emission of $\mathbf{L^3}$ at room temperature (298 K) and as a frozen glass (77 K).

Emission Spectroscopy. Various adducts of the three ligands were studied at room temperature and 77 K, and those of $\mathbf{L^3}$ are shown as an example in Figure 5. Emission of the free ligands $\mathbf{L^2}$, $\mathbf{L^3}$, and $\mathbf{L^4}$ in CH_3CN were measured at 298 and 77 K by exciting directly into the naphthalene $S_0 \rightarrow S_3$ band at ca. 225 nm. At 298 K, weak fluorescence for $\mathbf{L^2}$ and $\mathbf{L^3}$ was observed with a maximum at ca. 335 nm while no emission at all of $\mathbf{L^4}$ was found. Excitation into the lower-energy $S_0 \rightarrow S_2$ band gave identical results but with lower intensities, as nonradiative relaxation to the lowest-energy singlet excited-state precedes fluorescence.

In the 77 K frozen solution spectrum, the emission intensity was found to increase by 2 orders of magnitude for all three ligands in their free-base forms. Although an increase in intensity is to be expected due to the suppression of nonradiative pathways, the fluorescence enhancement in this case is more likely to be indicative of a room-temperature PET quenching reaction. As is the case with similar molecules,[29] amine lone pairs act as electron donors to reductively quench the naphthalene excited state. The enhanced fluorescence quenching of $\mathbf{L^4}$ at room temperature compared with that of $\mathbf{L^2}$ and $\mathbf{L^3}$ under the same conditions is presumably a result of the structural constraints imposed by the imidazolidine ring, resulting in the close proximity of several amine lone pairs that are able to reductively quench the naphthalene excited state. Both $\mathbf{L^2}$ and $\mathbf{L^3}$ have a greater degree of conformational flexibility, allowing faint emission to be observed from the naphthalene fragment, even at room temperature.

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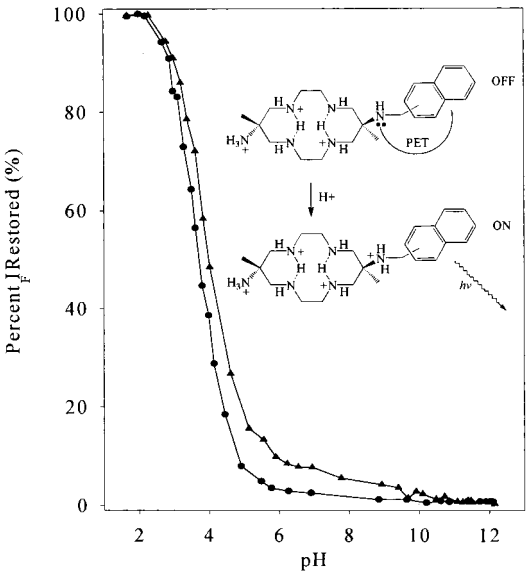

Figure 6. Variation in fluorescence intensity (I_F) at 335 nm with pH for the $\mathbf{L^2}$ (●) and $\mathbf{L^3}$ (▲) ligands in aqueous solution. Inset: protonation scheme responsible for observed PET quenching.

PET reactions that involve an amine lone pair as the electron donor can often be reversibly switched off by rendering the amine lone pair unavailable for photoinduced oxidation. Spectrofluorometric titrations of the fluorescence intensity at 335 nm (I_F) versus pH for each of the three ligands were performed in aqueous solution, the results of which are shown in Figure 6. Both $\mathbf{L^2}$ and $\mathbf{L^3}$ behaved similarly with full emission being restored at pH 3. Back-titrations of acidic solutions of $\mathbf{L^2}$ and $\mathbf{L^3}$ with aqueous sodium hydroxide resulted in a decrease in I_F that closely followed the plot of the initial titration experiments (data not shown). By contrast, the $\mathbf{L^4}$ ligand showed no discernible increase in emission intensity when an aqueous solution was acidified. The formation of a fine white precipitate as this titration progressed was noted, and this precipitate was subsequently identified by ^{1}H and ^{13}C NMR as 2-naphthaldehyde. Evidently, the imidazolidine undergoes hydrolysis in aqueous acidic conditions yielding the synthetic starting materials, both of which are nonluminescent at 335 nm. When similar experiments were performed using nonaqueous solutions (CH_3CN) and with trifluoroacetic acid (TFA) as the proton donor, the expected emission revival was observed for all three ligands and could be reversed by the addition of an organic base (e.g., Et_3N).

The I_F vs pH profiles in Figure 6 demonstrated an additional detail of the PET quenching reaction. Using the known protonation constants of the parent ligand, $\mathbf{L^1}$, as a guide, and noting that emission does not significantly increase until the pH is in the range of 3−4, we suggest that the species in aqueous solution most likely to first show revived fluorescence is that of the form $[H_4\mathbf{L}^{\boldsymbol{n}}]^{4+}$ ($\boldsymbol{n} = 2, 3$). A comparison of protonation constants for 1-aminomethylnaphthalene (pK_a 7.75) and methylamine (pK_a 10.64) shows that the naphthalene moiety is electron withdrawing, reducing the basicity of the neighboring amine.[30] Hence, in solution, the primary amine will be protonated prior to the substituted amino nitrogen and the latter is most likely to be responsible for the bulk of the observed PET quenching in a neutral to alkaline solution (see inset, Figure 6). The remaining unprotonated macrocyclic secondary amines evidently do not significantly quench luminescence. This is not surprising as crystal structures of $\mathbf{L^1}$ and analogues[31,32] in their protonated forms have shown that these secondary amines form very strong intramolecular hydrogen bonds with their adjacent ammonium groups.

Titrations of $\mathbf{L^2}$, $\mathbf{L^3}$, and $\mathbf{L^4}$ as their free bases with $Zn(OAc)_2$ in CH_3CN were also performed to generate the Zn(II) complexes in situ. A strong enhancement of fluorescence, which plateaued after the addition of 1 molar equiv of Zn(II), was observed in all three cases. Since these complexes display no absorption maxima to lower energies of the naphthalene chromophore and are also redox inactive, they are unable to quench emission by either an EET or a PET pathway involving the metal. Thus, coordination of Zn(II) to the amine lone pairs switches off the room-temperature ligand-centered PET reaction and fluorescence returns. As is the case with the Zn(II) complex of the $\mathbf{L^1}$ parent macrocycle,[19] it appears likely that the substituted ligands adopt hexadentate coordination modes to Zn(II); otherwise, emission could still be quenched by PET reactions involving the pendant amines.

Room-temperature emission spectra of the Cu(II) complexes of $\mathbf{L^2}$, $\mathbf{L^3}$, and $\mathbf{L^4}$ were measured in CH_3CN and were featureless. Titrations of these copper(II) complexes with CF_3COOH to generate the protonated species, $[Cu(H\mathbf{L}^{\boldsymbol{n}})]^{3+}$ and $[Cu(H_2\mathbf{L}^{\boldsymbol{n}})]^{4+}$ ($n = 2-4$), also resulted in a negligible increase in naphthalene emission. Thus, in contrast to their free-base forms, the noncoordinated amine lone pairs in the Cu(II) complexes do not seem to play an important role in their solution photochemistry. The observed emission quenching was similarly evident at 77 K in each case, which we take as being indicative of a temperature-independent EET quenching mechanism involving the naphthalene chromophore and the metal center.

Pulse Radiolysis. Reduction of the free ligands of $\mathbf{L^2}$ and $\mathbf{L^3}$ was achieved by pulse radiolytically generated aquated electrons and, in both cases, resulted in the appearance of an intense absorption at ca. 335 nm attributable to the naphthalenide radical anion (Supporting Information, Figure 1).[33] These peaks were absent in the spectra of the radiolytically reduced Cu(II) complexes indicating that reduction takes place at the Cu(II) center. Direct evidence for metal-centered reduction via the expected bleaching of the d−d band was not observed due to the limited sensitivity of the instrument.

Oxidation of the free ligands of $\mathbf{L^2}$ and $\mathbf{L^3}$ with $^{\bullet}$OH resulted in the appearance of strong absorptions at ca. 325 and 385 nm attributable to both the radical cation of the naphthalene moiety and a hydroxyl adduct (Supporting Information, Figure 1).[33,34] By contrast, the Cu(II) complexes yielded a single broad absorption centered at 380−390 nm attributable to the Cu(III) species by comparison with the known spectrum[13] of $[Cu(\mathbf{L^1})]^{3+}$ obtained by radiolytic oxidation of the parent complex, $[Cu(\mathbf{L^1})]^{2+}$. As noted earlier, the free ligand $\mathbf{L^4}$ is susceptible to aqueous hydrolysis and was not measured due to its instability in aqueous solutions.

Conclusions

A number of novel cyclam-based ligands bearing a pendant naphthalene group as a photoactive chromophore have been synthesized and characterized. As shown by their structural characterization, electronic spectra, and electrochemical behav-

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ior, the properties of the cyclam core remain relatively unaffected in $[Cu(\mathbf{L^2})]^{2+}$ and $[Cu(\mathbf{L^3})]^{2+}$ whereas they differ significantly for $[Cu(\mathbf{L^4})]^{2+}$ due to substitution at the donor atoms.

Variable-temperature emission spectroscopy has allowed the elucidation of the quenching mechanism operating in both the copper complexes and the free bases of these macrocycles. As their free base forms, the characteristic naphthalene emission is quenched by a PET reaction involving proximate amine lone pairs as electron donors. By contrast, the copper complexes of these ligands are quenched via an EET mechanism. Systematic variation of the separation between the copper(II) center and the naphthalene moiety achieved by synthetic variation had little effect on the efficiency of the EET quenching mechanism in solution. This is due to the exceptional quenching efficiency of the Cu(II) ion.

Thermodynamic calculations such as the free-energy changes associated with electron-transfer reactions are dependent on the intramolecular donor−acceptor separation. The hazards of using information gained from the solid state to interpret behavior in solution have been highlighted by the polymorphic crystal structures of $[Cu(\mathbf{L^2})^{2+}]$, which display significant changes in the naphthalene moiety's position with respect to the metal. Unless the solution structure is known to replicate that found in the solid state, as would be the case for the conformationally constrained $[Cu(\mathbf{L^4})](ClO_4)_2$ complex, the exact distance from the photoactive chromophore to the metal cannot be well defined in these and similar structures.

Our efforts are now turning toward the synthesis of electron and energy transfer reagents that incorporate a photoactive donor and a suitable acceptor at the opposing end of the $\mathbf{L^1}$ macrocycle, potentially facilitating a system with products that can be mediated by a metal center bound to the cyclam core.

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Supporting Information Available: Crystallographic data in CIF format, electronic spectra for selected free ligands and their Cu(II) complexes, and electronic spectra of selected pulse radiolysis products. This material is available free of charge via the Internet at http://pubs.acs.org.

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