Luminescence studies of copper(I)-containing [2]pseudorotaxanes

Breeze N. Briggs, Fabien Durola, David R. McMillin, and Jean-Pierre Sauvage

Abstract: This report describes photoluminescence studies of copper-containing [2]pseudorotaxanes that mimic elements of functioning molecular machines. Excitation with visible light induces a formal oxidation of the metal center and simulates an actuation process. In all four [2]pseudorotaxanes studied, the ring ligand is the same, but the thread ligand is variable, namely 2,9-di(anisol-4-yl)-1,10-phenanthroline (dap), 6,6′-di(anisol-4-yl)-2,2′-bipyridine (o-dabipy), 5,5′-di(anisol-4-yl)-2,2′-bipyridine (m-dabipy), or 8,8′-di(anisol-4-yl)-3,3′-bi-isoquinoline (dabiiq). The absorbance bandshapes suggest that aryl substituents extending from the core ligands engage in stacking interactions and induce a partially flattened structure in the ground state. More severe flattening occurs in the excited state and precludes the observation of emission if interligand steric forces do not limit the distortion. Thus, the [2]pseudorotaxanes containing dap or o-dabipy as the thread ligand exhibit uncorrected emission maxima at around 720 nm in room-temperature dichloromethane, while the less constrained analogues, containing dabiiq or m-dabipy, are not emissive in fluid solution and barely exhibit a signal in rigid media. In dichloromethane, the luminescence quantum yields of the dap- and o-dabipy-containing systems are 6×10^{-4} and 4×10^{-4}, and the excited-state lifetimes are 98 ns and 90 ns, respectively.

Key words: copper(I), luminescence, rotaxane, charge transfer.

Résumé : On a effectué des études de photoluminescence de [2]pseudorotaxanes contenant d cuivre et qui imitent les éléments de machines moléculaires opérationnelles. L’excitation à l’aide de lumière visible induit une oxydation formelle du centre métallique et simule un processus d’activation. Dans les quatre [2]pseudorotaxanes étudiés, le noyau du ligand est le même, mais le ligand commun est variable, soit la 2,9-di(anisol-4-yl)-1,10-phénanthroline (dap), la 6,6′-di(anisol-4-yl)-2,2′-bipyridine (o-dabipy), la 5,5′-di(anisol-4-yl)-2,2′-bipyridine (m-dabipy) et la 8,8′-di(anisol-4-yl)-3,3′-biisoquinoléine (dabiiq). Les formes des bandes d’absorption suggèrent que les substituants aryles qui s’orientent vers l’extérieur des ligands de coeur donnent lieu à des interactions d’empilement et qu’ils induisent une structure partiellement aplatie dans l’état fondamental. Un aplatissement plus important se produit dans l’état excité et il empêche l’observation de l’émission si les forces stériques inter-ligand ne limitent pas la distorsion. Ainsi, les [2]pseudorotaxanes qui contiennent du « dap » ou du « o-dibipy » comme ligand commun donnent lieu à des maxima d’émission non corrigée autour de 720 nm, à la température ambiante, dans le dichlorométhane, alors que les analogues avec moins de contraintes, contenant du « dabiiq » ou du « m-dapiry » ne donnent pas lieu à de l’émission en solution fluide et ils présentent à peine un signal en milieu solide. Dans la dichlorométhane, les rendements quantiques de luminescence des systèmes contenant du « dab » ou du « o-dabipy » sont de 6×10^{-4} et 4×10^{-4} et les temps de vie des états excités sont respectivement de 98 et 90 ns.

Mots-clés : cuivre(I), luminescence, rotaxane, transfert de charge.

[Traduit par la Rédaction]

Introduction

Copper(I) is a useful templating agent for the synthesis of molecules exhibiting interesting topologies.[1] An example is a two-component molecular assembly known as a [2]rotaxane, which threads together like an axle through a wheel. Elaborate versions can function as molecular machines, i.e., molecular device prototypes that execute mechanical motion in response to an external input.[2–4] For example, a copper-containing [2]rotaxane with 1,10-phenanthroline and 2,2′:6′,6″-terpyridine stations in the ring ligand is capable of displaying rotary motion, as recently demonstrated by Raehm et al.[5] Electrochemical actuation is possible because the copper(I) and copper(II) oxidation states characteristically prefer different coordination numbers. Thus, the thermodynamically favored copper(I) form is four-coordinate and

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entails complexation to the phenanthroline embedded in the ring component. Upon oxidation of the copper center, the metal prefers to be five-coordinate, hence the ring ligand pirouettes about the thread and coordinates to the metal via the terpyridine moiety.[5] Regeneration of the phenanthroline-bound form occurs with reduction back to copper(I).

Photoluminescence studies are potentially relevant to the dynamics of the system because population of the emitting metal-to-ligand charge-transfer (MLCT) excited state entails formal oxidation of the metal center.[6–9] In general, two important structural changes occur in a Cu(NN)$_2^+$ system after absorption to the Franck–Condon state. (Herein, NN designates a diimine ligand such as 1,10-phenanthroline or 2,2′-bipyridine). First, the excited state undergoes a flattening distortion,[7–11] which is complete in less than a picosecond.[12,13] Subsequently, at least in donor media, expansion of the coordination number and solvent-induced exciplex quenching occurs on a nanosecond time scale.[12,13] There are, however, few reports about luminescence studies involving copper(I)-containing [2]rotaxanes and related systems.[14] Most of the work focuses on systems designed to produce charge separation. Armaroli et al.[15] have, for example, studied a copper(I)-containing [2]rotaxane that incorporated a bis(1,10-phenanthroline) ligand environment for the metal center as well as bulky C_{60} groups as termini at both ends of the thread ligand. They find that photoexcitation induces net electron transfer from the copper center to a C_{60} and virtually complete quenching of the CT emission from the copper center as well as the fluorescence from the C_{60} unit.[15] Using a related structure, which included a zinc porphyrin as well, Li et al. have detected MLCT luminescence from the bis(1,10-phenanthroline)copper center, but the lifetime is very short due to oxidative quenching by C_{60} acceptors.[16]

For convenience, the emission studies described below utilize [2]pseudorotaxanes, which lack the bulky “stopper” groups that prevent unthreading in a true [2]rotaxane. Figure 1 shows the structure of the m-30 ring ligand, which all systems have in common. The thread component is any one of four different ligands also depicted in Fig. 1, namely 2,9-di(anisol-4-yl)-1,10-phenanthroline (dap), 6,6′-di(anisol-4-yl)-2,2′-bipyridine (o-dabipy), 5,5′-di(anisol-4-yl)-2,2′-bipyridine (m-dabipy), or 8,8′-di(anisol-4-yl)-3,3′-bi-isoquinoline (dabiiq).

Experimental

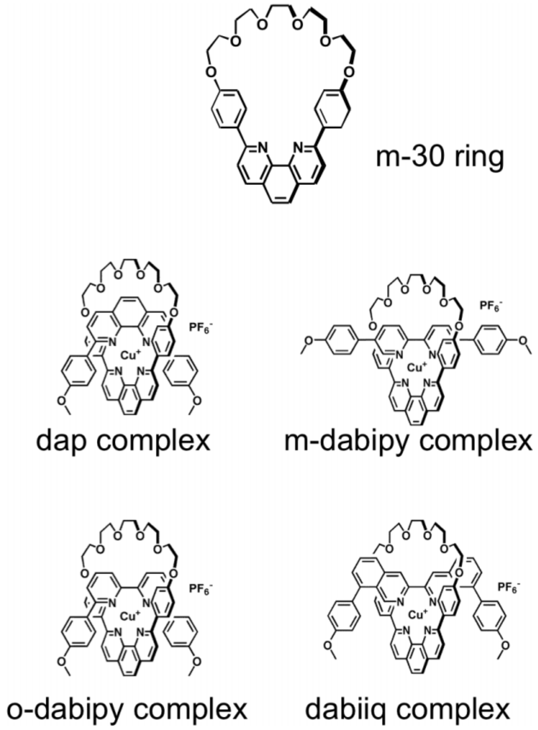
Synthesis

Previously published procedures yielded the coordinating macrocycle m-30[17] and the ligands dap,[18] o-dabipy,[19] and dabiiq.[20]

5,5′-Dianisyl-2,2′-bipyridine (m-dabipy)

The 5,5′-dibromo-2,2′-bipyridine precursor[21] (150 mg, 0.32 mmol), 4-methoxyphenyl boronic acid (106 mg, 0.704 mmol), and Na_2CO_3 (675 mg, 6.4 mmol) were placed in a two-necked round-bottom flask under argon. Then, toluene (30 mL), deionized water (10 mL), and ethanol (5 mL) were added. The solution was degassed and stirred under argon, then $Pd(PPh_3)_4$ (37 mg, 0.032 mmol) was added. The mixture was then degassed again and stirred at 90 °C for 16 h. Solvents were evaporated and a poorly soluble product was obtained. The crude product was thoroughly washed with water to remove sodium carbonate. The product was then washed five times with CH_2Cl_2 to remove starting material and soluble byproducts. The title product was thus obtained pure as a white solid (54 mg, 46% yield).

Fig. 1. Copper-containing [2]pseudorotaxanes studied along with m-30 the ring ligand for each.



^{1}H NMR (DMSO-d_6, 300 MHz): δ (ppm) = 9.00 (d, 2H, J = 2.3 Hz), 8.45 (d, 2H, J = 8.3 Hz), 7.93 (dd, 2H, J = 8.3, 2.3 Hz), 7.79 (d, 4H, J = 8.8 Hz), 7.10 (d, 4H, J = 8.8 Hz), 3.84 (s, 6H).

Threaded complexes: Cu(m-30)(NN)$^+$ PF$_6^-$

In a typical procedure, $Cu(CH_3CN)_4PF_6$ (1 equiv.) in degassed CH_3CN (0.5 mL per mg of complex) was added to a stirred degassed solution of macrocycle m-30 (1 equiv.) in CH_2Cl_2 (0.3 mL per mg of m-30). A deep orange color appeared instantly. A short while later, a solution in CH_2Cl_2 (0.3 mL per mg ligand) of 1 equiv. of the diimine ligand (NN, respectively, dap, o-dabipy, m-dabipy, or dabiiq) was added at room temperature, and the solution immediately turned dark red. After the solution was stirred for 2 h under argon at room temperature, the solvents were removed under vacuum. The dark red solid thus obtained was dissolved again in a minimum of degassed CH_3CN. As a precaution, the solution was filtered, after which evaporation of the filtrate yielded the copper complex quasi-quantitatively.

Cu(m-30)(dap)$^+$ PF$_6^-$

^{1}H NMR (CD_3CN, 300 MHz): δ (ppm) = 8.65 (d, 2H, J = 8.4 Hz), 8.55 (d, 2H, J = 8.4 Hz), 8.25 (s, 2H), 8.09 (s, 2H), 7.92 (d, 2H, J = 8.4 Hz), 7.88 (d, 2H, J = 8.4 Hz), 7.55 (d, 4H, J = 8.7 Hz), 7.34 (d, 4H, J = 8.7 Hz), 6.09 (d, 4H, J = 8.8 Hz), 6.01 (d, 4H, J = 8.8 Hz), 3.82 (s, 4H), 3.73–3.70 (m, 4H), 3.60–3.57 (m, 4H), 3.55–3.51 (m, 4H), 3.46 (s, 6H), 3.44–3.41 (m, 4H). ES-MS *m*/*z* = 1021.3218 (calcd. 1021.3238 for $C_{60}H_{54}CuN_4O_8^+$).

Cu(m-30)(o-dabipy)⁺ PF₆⁻

^{1}H NMR (CD_3CN, 300 MHz): δ (ppm) = 8.50 (d, 2H, *J* = 8.4 Hz), 8.27 (d, 2H, *J* = 8.0 Hz), 8.10 (t, 2H, *J* = 8.0 Hz), 8.02 (s, 2H), 7.90 (d, 2H, *J* = 8.4 Hz), 7.56 (d, 2H, *J* = 8.0 Hz), 7.54 (d, 4H, *J* = 8.8 Hz), 7.39 (d, 4H, *J* = 8.8 Hz), 6.44 (d, 4H, *J* = 8.8 Hz), 6.00 (d, 4H, *J* = 8.8 Hz), 4.02–3.99 (m, 4H), 3.76 (s, 4H), 3.74 (br, 8H), 3.73–3.70 (m, 4H), 3.36 (s, 6H). ES-MS *m*/*z* = 997.3212 (calcd. 997.3238 for $C_{58}H_{54}CuN_4O_8^+$).

Cu(m-30)(m-dabipy)⁺ PF₆⁻

^{1}H NMR (CD_3CN, 300 MHz): δ (ppm) = 8.74 (d, 2H, *J* = 8.4 Hz), 8.29–8.16 (m, 10H), 7.55 (d, 8H, *J* = 8.6 Hz), 7.06 (d, 4H, *J* = 8.6 Hz), 6.27 (d, 4H, *J* = 8.6 Hz), 3.85 (s, 6H), 3.82–3.79 (m, 4H), 3.78 (s, 4H), 3.77–3.74 (m, 4H), 3.69–3.66 (m, 4H), 3.65–3.62 (m, 4H). ES-MS *m*/*z* = 997.3207 (calcd. 997.3238 for $C_{58}H_{54}CuN_4O_8^+$).

Cu(m-30)(dabiiq)⁺ PF₆⁻

^{1}H NMR (CD_3CN, 300 MHz): δ (ppm) = 9.04 (s, 2H), 8.69 (d, 2H, *J* = 8.4 Hz), 8.63 (s, 2H), 8.18 (d, 2H, *J* = 8.3 Hz), 8.14 (s, 2H), 8.10 (d, 2H, *J* = 8.4 Hz), 7.93 (dd, 2H, *J* = 8.2, 7.2 Hz), 7.60 (d, 2H, *J* = 7.1 Hz), 7.49 (d, 4H, *J* = 8.8 Hz), 7.26 (d, 4H, *J* = 8.8 Hz), 6.92 (d, 4H, *J* = 8.8 Hz), 6.15 (d, 4H, *J* = 8.8 Hz), 3.87 (s, 4H), 3.77 (s, 6H), 3.76–3.73 (m, 4H), 3.65–3.62 (m, 4H), 3.58–3.55 (m, 4H), 3.48–3.44 (m, 4H). ES-MS *m*/*z* = 1097.3534 (calcd. 1097.3551 for $C_{66}H_{58}CuN_4O_8^+$).

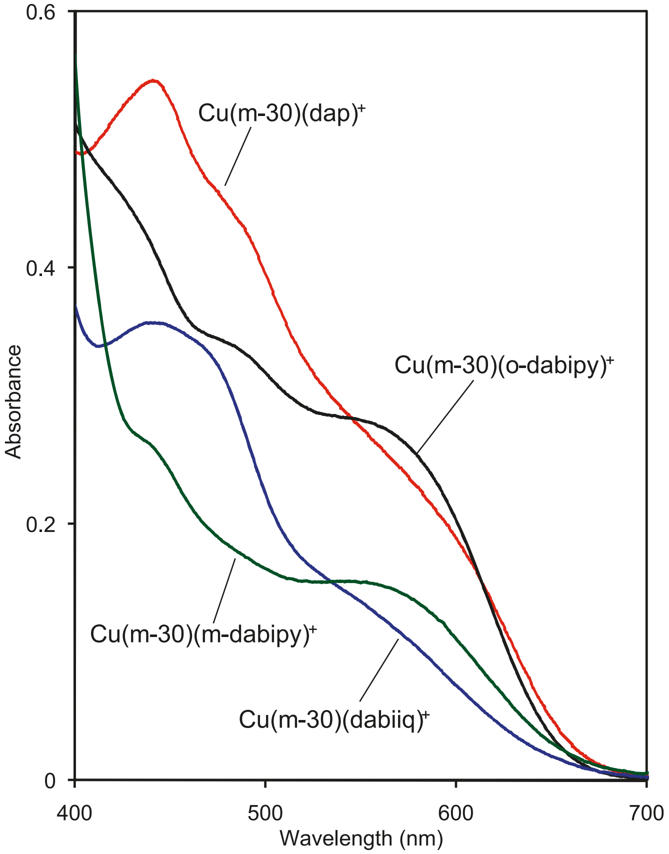
Methods

In the emission studies involving solid-state or frozen-glass samples, a 620 nm long-pass filter was in place to reject scattered light. The excitation beam also passed through a notch filter centered at 450 nm. For excitation and emission, the slit settings were 10 nm and 20 nm, respectively. The glassing solvent was a 4:1 mixture of ethanol:methanol, and the sample holder was a 3 mm i.d. quartz tube immersed in a finger dewar filled with liquid nitrogen. The same assembly without cryogen also allowed for measurements from solid-state samples. For frozen glass and solid-state emission measurements, the blank was either an empty capillary tube or one loaded with a non-emissive, solid-state copper(I) compound. The procedure for deoxygenation of dichloromethane entailed a sequence of freeze–pump–thaw cycles. For lifetime measurements, a combination of 620 and 700 nm long pass filters prevented scattered light from impinging on the detector. The setup also included a 450 nm notch filter in the laser beam. The laser dye was Coumarin 440 in ethanol at a concentration of 6.1×10^{-3} mol/L. The method of Parker and Rees yielded estimates of emission quantum yields.[22] Residual solvent protons (^{1}H NMR: CD_3CN: 1.96 ppm, DMSO-d_6: 2.50 ppm) served for referencing NMR signals.

Instrumentation

The spectrophotometer for the absorbance measurements was a Varian Cary 300 Bio unit. A Varian Cary Eclipse unit yielded photoluminescence data. A description of the apparatus used for the lifetime measurements is in the literature.[23] The NMR spectrometer was a Bruker AVANCE 300 (300 MHz). The mass spectrometer was a Bruker MicroTOF (ES-MS).

Fig. 2. Absorbance spectra of dap, o-dabipy, dabiiq, and m-dabipy complexes in dichloromethane at room temperature.



Results

The solvent employed for most of the solution work was dichloromethane (DCM) wherein the four copper complexes exhibit the visible absorption spectra depicted in Fig. 2. In each case, a strong, variably structured absorption occurs in the vicinity of 450 nm along side a broad shoulder that appears at ~580 nm. The shoulder is especially prominent in the spectra of the o-dabipy and m-dabipy complexes. Despite similar absorption throughout the series, only the dap and o-dabipy complexes exhibit a detectable emission signal in room-temperature solution. The emission is broadband in both cases and maximizes between 710 nm and 720 nm (Table 1); see Fig. 3 for data pertaining to the o-dabipy complex. In deoxygenated DCM at room temperature, the luminescence quantum yields are 6×10^{-4} and 4×10^{-4} for the dap and o-dabipy complexes, respectively. The corresponding emission lifetimes are 98 ns and 90 ns. In an alcohol glass at 77 K, the same two complexes exhibit an emission maximum at about 740 nm, and the lifetime of the emission signal extends considerably to 990 ns for the dap complex and 870 ns for the o-dabipy analogue. In the frozen glass, the dabiiq and m-dabipy complexes also emit, though very weakly, and exhibit lifetimes of 185 ns and 155 ns, re-

Table 1. Emission data for Cu(m-30)(NN)$^+$ systems.

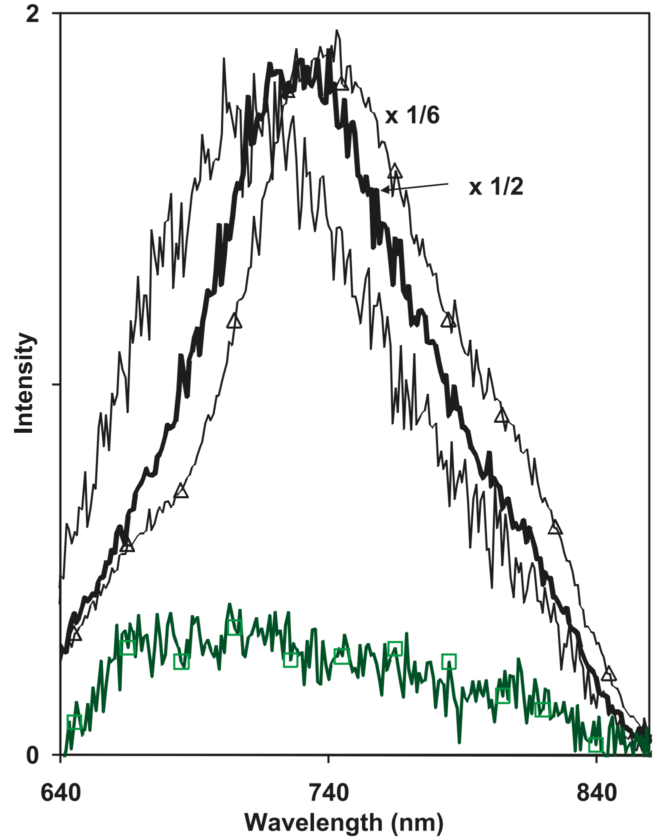
	λ[a] nm (τ, ns)		
Complex	298 K in DCM[b]	77 K in EtOH/MeOH	298 K in solid state
Cu(m-30)(dap)$^+$	718 (98)	745 (990)	720 (270)
Cu(m-30)(o-dabipy)$^+$	715 (90)	740 (870)	730 (150)
Cu(m-30)(m-dabipy)$^+$	—[c]	760 (155)	770 (—[c])
Cu(m-30)(dabiiq)$^+$	—[c]	760 (185)	770 (—[c])

[a] From uncorrected spectra.

[b] Quantum yields: dap complex 6.4×10^{-4}; o-dabipy complex 4.0×10^{-4}.

[c] Not resolved.

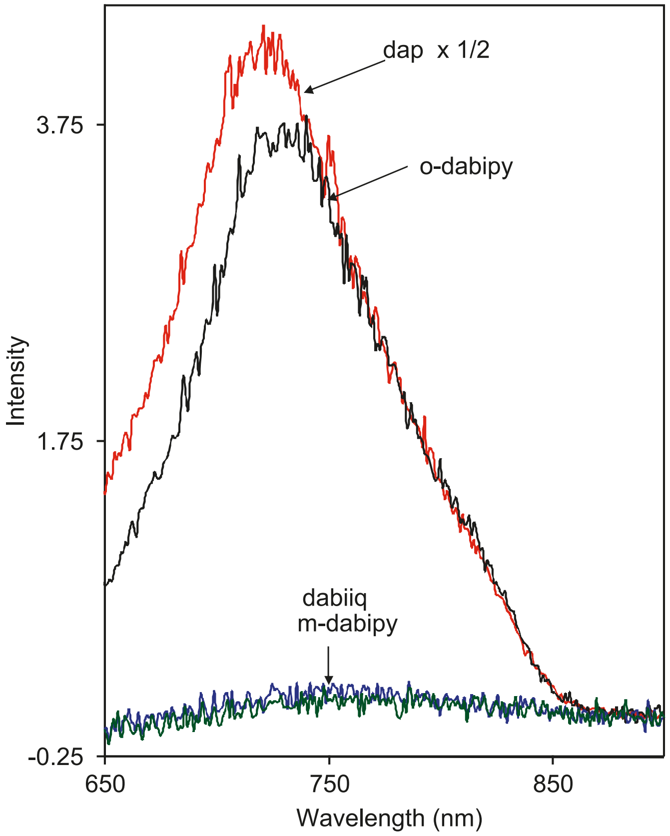
Fig. 3. Uncorrected emission spectra of the hexafluorophosphate salt of Cu(m-30)(o-dabipy)$^+$ measured in room-temperature dichloromethane (thin), the solid state (thick × 1/2), as well as a 77 K alcohol glass (-Δ- × 1/6), and from the corresponding salt of Cu(m-30)(m-dabipy)$^+$ in an alcohol glass at 77 K (-□-). Emission intensities are arbitrary.



spectively. See Fig. 3 for the 77 K spectrum of the [2]pseudorotaxane with m-dabipy as the thread ligand. The emissions from the dap and o-dabipy complexes are both much more intense and durable enough to persist in the weakly basic solvent acetonitrile at room temperature, although the lifetimes contract to 50 ns and 30 ns, respectively.

The emission results are qualitatively similar in the solid state; see Fig. 4. In the case of the dap complex, the solid-state emission spectrum virtually coincides with that obtained in room-temperature, fluid solution, but the lifetime extends to 270 ns. On the other hand, the emission maximum for the o-dabipy complex shifts to slightly longer wavelength (730 nm), and that may account for the smaller increase in the emission lifetime (to 150 ns). Figure 4 shows that the dabiiq and m-dabipy complexes both exhibit weak emissions, centered at ~770 nm in the solid state. Unfortunately, neither signal is strong enough to permit a lifetime measurement.

Fig. 4. Uncorrected emission spectra measured from solid samples of [Cu(m-30)(dap)]PF$_6$, [Cu(m-30)(o-dabipy)]PF$_6$, [Cu(m-30)(m-dabipy)]PF$_6$, and [Cu(m-30)(dabiiq)]PF$_6$ at room temperature.

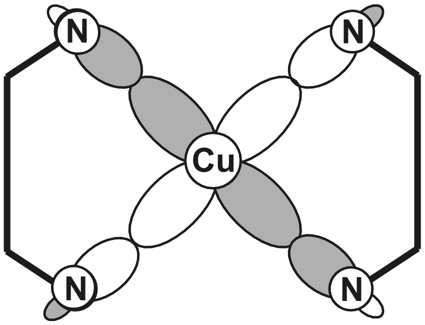


Discussion

CT absorption and emission

Previous work has shown that the MLCT excitation that dominates the visible spectrum of a Cu(NN)$_2^+$ complex originates in the dπ orbitals of the metal that have nonzero overlap with empty π*(NN) acceptor orbitals of the ligand.[24,25] The presence of ligands with chemically distinct π systems in the thread and ring components may introduce

Fig. 5. Schematic view of bonding overlap formed by the half-occupied dσ orbital of a copper(II) center and the donor orbitals of two α,α-diimine ligands in the limit of a planar coordination geometry.



a broadening of the visible spectrum. Moreover, the shoulders that appear at λ ~575 nm in Fig. 2 are *characteristic* of $Cu(NN)_2^+$ systems in which at least one of the ligands has an aryl substituent positioned ortho to one or both of the imine nitrogens.[26,27] The shoulders result from two distinct *ground-state* distortions that destroy idealized D_{2d} symmetry and split the dπ orbital energies.[28–30] One is a "rocking" distortion that imparts a pyramidal coordination geometry, probably promoted by the formation of a stacking interaction involving an aryl substituent on one ligand and the aromatic core of the opposite ligand.[29] The second distortion entails a tetragonal flattening of the N_4 donor set about the copper center.[30] For the latter distortion, the driving force is presumably the mesomeric interaction(s) that results (result) when the aryl substituent(s) adopts (adopt) smaller dihedral angle(s) relative to the mean plane of the NN ligand.[30] Significant flattening is possible with a very modest driving force because the major opposing force derives from interligand steric interactions when the central ion is a d^{10} closed-shell metal center. The same interactions account for notable differences in the formation constants of $Cu(NN)^+$ and $Cu(NN)_2^+$ systems with aryl- as opposed to alkyl-substituted NN ligands.[31]

Further structural changes occur in the MLCT excited state due to the d-shell vacancy created, another consequence of which is the shift in the X-ray absorption edge of the copper center.[12] Nominally containing copper(II), the thermally equilibrated excited state becomes even more flattened, as a consequence of a second-order Jahn–Teller effect.[11] In more descriptive terms, additional flattening occurs because it leads to improved overlap amongst sigma-donor orbitals of the ligand and the half-occupied d orbital of copper in the CT excited state (Fig. 5). Indeed, the same kind of flattening is evident in the structures of oxidized $Cu(NN)_2^{2+}$ analogues.[32,33] When the flattening is severe, as in the case of $Cu(phen)_2^+$, the excited-state potential energy surface may impinge on the ground-state surface. The emission yield then becomes vanishingly small due to efficient non-radiative decay, even in frozen solution.[34,35] Indeed, for a $Cu(NN)_2^+$ system to exhibit emission in solution, sterically active groups must be present adjacent to the donor nitrogens to limit the extent of flattening.[7,9,36]

Within the [2]pseudorotaxane series studied herein, the m-30 ring ligand is a key structural element that clearly has a salutary effect on the emission lifetime of the o-dabipy complex (90 ns in DCM). Normally, $Cu(NN)_2^+$ complexes based on 2,2′-bipyridine ligands have relatively short-lived excited states, e.g., 34 ns for Cu(6,6′-diphenyl-4,4′-dimethyl-2,2-bipyridine)$_2^+$.[33] For comparison, the corresponding excited-state lifetime is 310 ns for Cu(2,9-diphenyl-4,7-dimethyl-1,10-phenanthroline)$_2^+$.[37] Ligand-dependent distortions may account for the difference in lifetimes of the two controls, especially torsional relaxation about the 2,2′ bond of the bipyridine ligand. In each case, bond length changes also occur in the excited state due to population of a π* orbital of the ligand. Bond length changes are apt to be greater in a bipyridine complex because the π* orbital delocalizes over fewer atoms than is the case with a phenanthroline moiety. One possibility is that the structural changes are less important in the o-dabipy-containing [2]pseudorotaxane because the CT excitation actually localizes on the m-30 ring ligand. In line with this possibility, the emission occurs at about the same energy whether the thread ligand is dap or o-dabipy. The m-30 ring ligand is no panacea, however, because the bis-thread complex $Cu(dap)_2^+$ exhibits a *longer* excited-state lifetime (260 ns[26]) than the dap-containing [2]pseudorotaxane. Vibrationally assisted radiationless decay may be less efficient for $Cu(dap)_2^+$ if the absence of a ring ligand permits better nesting of the ground- and excited-state potential energy surfaces.

Moreover, the m-30 ligand is not sufficiently structure-preserving to permit a photoluminescence signal if fluid solution from the [2]pseudorotaxane containing either m-dabipy or dabiiq as the thread ligand. In both cases, the anisole substituents of the thread ligand are evidently far enough removed from the opposite m-30 ligand that appreciable flattening occurs in the excited state and quenches the emission. Even in the solid state, where packing forces can come into play and help preserve structure,[11] the emissions from the m-dabipy and dabiiq complexes are very weak and maximize at relatively long wavelengths.

In summary, absorbance bandshapes reveal that all of the [2]pseudorotaxanes studied adopt low symmetry, partially flattened structures due to intra- and inter-ligand interactions involving bulky anisole substituents. Sterically active ligand substituents must be present to inhibit a flattening distortion in the excited state that quenches the photoluminescence. However, the steric interactions may produce inter-ligand "friction" that affects the mechanical response time. In fact, the [2]pseudorotaxanes that contain either the relatively open dabiiq or m-dabipy ligand (and exhibit faster mechanical motion[38]) are non-luminescent in room-temperature dichloromethane solution, whereas the dap and o-dabipy analogues exhibit emissions that maximize at ~720 nm and decay with time constants of 98 ns and 90 ns, respectively. The lifetime for the Cu(m-30)(o-dabipy)$^+$ system is more than twice what one would expect for a simple bis-bipyridine analogue. At 77 K in a frozen glass, the decay times for the emissions from Cu(m-30)(dap)$^+$ and Cu(m-30)(o-dabipy)$^+$ extend to almost a microsecond, whereas in room-temperature acetonitrile solution, the same complexes undergo solvent-induced exciplex quenching on a time scale of just under a microsecond, according to lifetime data.

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