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Diastereoselective Formation and Photophysical Behavior of a Chiral Copper(I) Phenanthroline Complex

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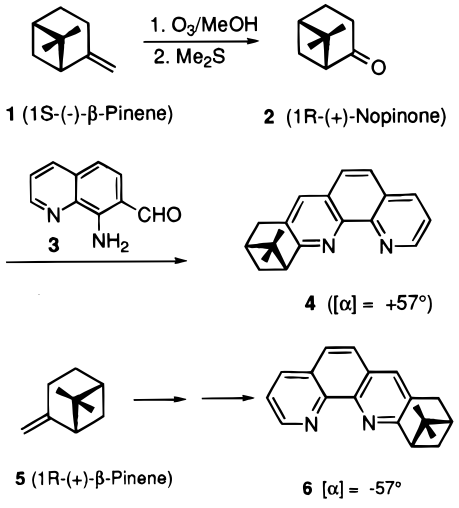
The Friedländer condensation of (1*R*,5*S*)-(+)- and (1*S*,5*R*)-(−)-nopinone with 8-aminoquinoline-7-carbaldehyde leads to the corresponding enantiomerically pure (2,3-*b*)-pineno-1,10-phenanthrolines. Coordination of these ligands with Cu(I) affords non-interconvertable chiral complexes which show equal and opposite Cotton effects in their CD spectra as well as identical half-wave oxidation potentials of +0.37 V and identical MLCT absorptions at 442 nm. Both complexes are nonemissive at 298 and 77 K. Stern−Volmer quenching studies were carried out with optically pure Δ- and Λ-$[Ru(bpy)_3]^{2+}$ and racemic $[Ru(dpb)_3]^{2+}$ as donors (bpy = 2,2′-bipyridine and dpb = 4,4′-diphenyl-bpy). Neither study provides any evidence of enantioselective quenching, indicating that energy or electron transfer may be occurring through a distance where chiral recognition is unimportant.

The 1,10-phenanthroline (phen) nucleus has been widely employed as a ligand for Cu(I). Oxidative instability evidenced by complexes of the parent ligand can be moderated by the introduction of 2,9-substituents that provide steric inhibition to the planarization which would occur in conjunction with oxidation to a Cu(II) species. Considerable attention has thus been directed toward Cu(I) complexes of species such as 2,9-dimethyl-phen (dmp)[1] and 2,9-diphenyl-phen (dpp).[2] We have recently discovered that 2-phenyl-phen will form a stable Cu(I) complex and, in fact, phen derivatives with only one sterically encumbering substituent will accomplish this objective.[3]

Unlike symmetrically 2,9-disubstituted phens, the 2-substituted derivatives are asymmetric about the chelating moiety, and thus tetrahedral ML_2 complexes should exhibit chirality. Thus far, however, due to rapid ligand exchange in solution, we have been unsuccessful in efforts to resolve a racemic mixture similar to the one depicted in Figure 1.[4]

To circumvent this problem, we have now employed a chiral phen species which exhibits a high degree of diastereoselectivity in the formation of its $[CuL_2]^+$ complex. The enantiomeric ligands **4** and **6** were prepared by the Friedländer condensation of 8-amino-7-quinolinecarbaldehyde (**3**)[5] with either (1*R*,5*S*)-(+)- or (1*S*,5*R*)-(−)-nopinone. These ketones could, in turn, be derived in high enantiomeric purity from ozonolysis[6] of the corresponding readily available pinene enantiomers **1** and **5**.[7] The pair of phens, **4** and **6**, exhibited equal and opposite optical rotations, and analysis on a *β*-cyclodextrin chiral HPLC column gave base-line separation and indicated enantiomeric purities greater than 99%.



1 (1S-(-)-β-Pinene)

2 (1R-(+)-Nopinone)

3

4 ([α] = +57°)

5 (1R-(+)-β-Pinene)

6 [α] = -57°

The ligands **4** and **6** show certain advantages over other previously prepared chiral derivatives of phen[8] or 2,2′-bipyri-

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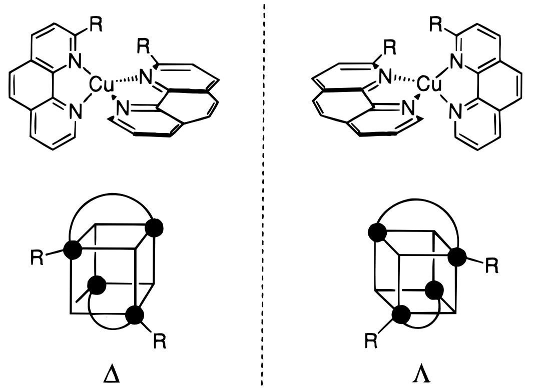
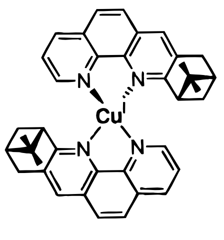
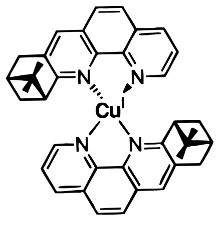


Figure 1. Chirality in [Cu(2-R-phen)$_2$]$^+$ complexes.

dine.[9] First, both enantiomers are readily available. Second, the chiral discrimination is quite significant, depending upon the difference between a $-CH_2-$ and a $-C(CH_3)_2-$. Finally, the chiral auxiliary is located close to the chelating moiety and, being fused to the phen rather than appended to it, provides a more predictable chiral environment.

When **4** is treated with 0.5 equiv of [Cu(CH$_3$CN)$_4$](ClO$_4$) in acetonitrile, a deep red solution is obtained which provides the crystalline [Cu(**4**)$_2$]$^+$ complex upon concentration. The 300 MHz ^{1}H NMR of this species shows one clear, well-resolved set of resonances, indicating the presence of a single stereoisomer. The two methyl groups appear as two three-proton singlets at 0.93 and 0.52 ppm, shifted upfield from where they occur in the free ligand (1.46 and 0.70 ppm). If one assumes that the coordination to form [Cu(**4**)$_2$]$^+$ occurs in a stepwise fashion, examination of a molecular model indicates that one of the two possible orientations for complexation of the second ligand would create a severe interaction between the *gem*-dimethyl groups of the orthogonal ligands. Thus **4** gives rise only to the Λ-isomer in which these groups point away from each other. Complexation of **6** in a similar manner again leads to a single stereoisomer now having the Δ-configuration and giving an NMR which is identical to the one obtained for [Cu(**4**)$_2$]$^+$.


Δ-[Cu(**6**)$_2$]$^+$ (Δ-Cu)


Λ-[Cu(**4**)$_2$]$^+$ (Λ-Cu)

Both complexes show completely superimposable IR and UV−vis spectra. Solutions of the complexes were not sufficiently transparent to allow measurement of their optical rotations, but we were able to measure their CD spectra, and both complexes showed equal and opposite Cotton effects in the region of MLCT absorption (Figure 2).

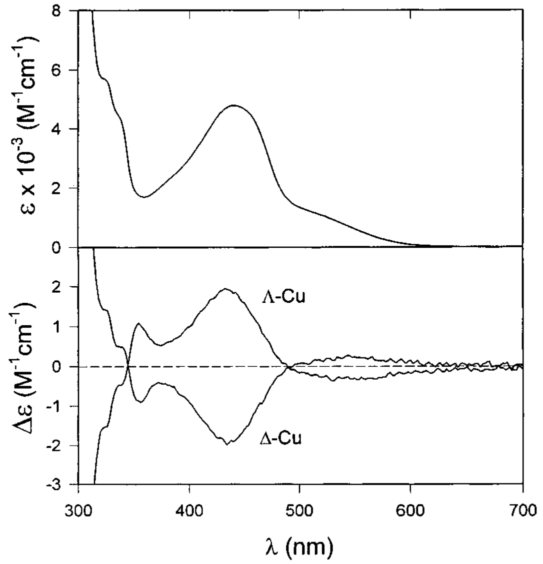


Figure 2. Absorption (top) and circular dichroism (bottom) spectra of Λ-Cu and Δ-Cu in CH$_2$Cl$_2$ solution at 298 K.

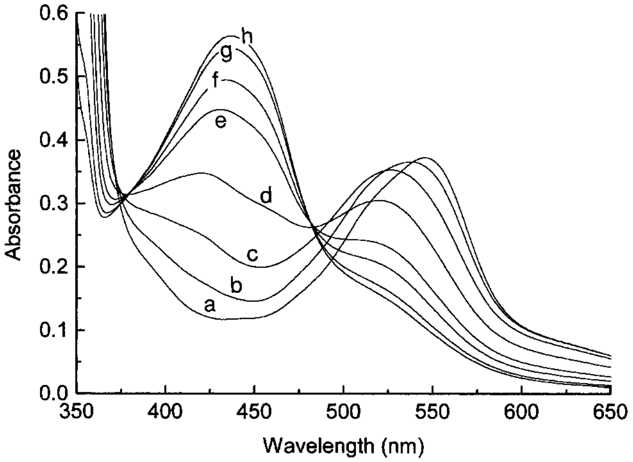


Figure 3. Electronic absorption spectra for [Cu(biq)$_2$](ClO$_4$) (1.02×10^{-2} M in CH$_3$CN) with varying number of equivalents of added ligand **4**: (a) pure [Cu(biq)$_2$](ClO$_4$); (b) 0.5; (c) 1.0; (d) 1.5; (e) 2.0; (f) 2.5; (g) 3.0; (h) 3.5.

The half-wave oxidation potentials for the complexes in acetonitrile were identical at +0.37 V (vs SCE), and the waves were quasi-reversible with an 80 mV difference between the anodic and cathodic peak potentials. These complexes are more easily oxidized than [Cu(dmp)$_2$]$^+$ ($E_{1/2}$(ox) = +0.67 V[10]). In general we have found that the oxidation potentials of monosubstituted phens are less sensitive to the steric bulk of the single substituent since a pathway for planarization exists which requires minimal interaction between the substituents on different ligands. For example, the 2,3-cyclohexeno-fused analogue of **4** and **6** which lacks the bulky *gem*-dimethyl bridge exhibits an $E_{1/2}$(ox) of +0.44 V.[11]

For series of Cu(I) complexes of 2,2′-biquinoline (biq) derivatives, we have recently demonstrated that the stability of the complex can be evaluated by spectroscopic monitoring of ligand exchange.[12] Since the MLCT absorptions for biq and phen complexes of Cu(I) occur at appreciably different wavelengths, the exchange of these ligands may be readily analyzed. Figure 3 shows a set of absorption curves generated as one adds incremental amounts of ligand **4** to a 1.02×10^{-4} M acetonitrile

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Table 1. Absorption and Luminescence Data of Some Cu(I) Bis-phen Complexes (CH_2Cl_2 Solution, 298 K)

	absorption		luminescence		
complex	$\lambda_{\max}$ (nm)	ϵ (M^{-1} cm^{-1})	$\lambda_{\max}$ (nm)	$10^4\Phi$	τ (ns)
$Cu(phen)_2^{+\,a}$	435	7000			
$Cu(dmp)_2^+$	454^b	7950^b	750^c	2.7^c	90^c
$Cu(dpp)_2^+$	441^a	3620^a	710^c	11^c	250^c
Δ-Cu	442	5700			
Λ-Cu	442	5700			

[a] Data from ref 13a. [b] Data from ref 13c. [c] Data from ref 13b.

solution of $[Cu(biq)_2](ClO_4)$. It is noteworthy that the addition of up to 1.5 equiv of **4**, illustrated by the first four curves, does not exhibit a clear isosbestic point due to the intermediacy of a mixed-ligand complex $[Cu(biq)(\mathbf{4})]^+$. The addition of greater than 1.5 equiv of **4** then provides a clear conversion of this species to the Λ-Cu complex.

Two factors govern the relative stabilities of phen and biq complexes of Cu(I). One factor is the steric hindrance to planarization exerted by 2- and 9-substituents on the phen or the benzo ring of biq. The other factor is flexibility of the 2,2′-bond of biq which allows for more facile stepwise ligand dissociation. For phen there is no such flexibility. For these reasons, we have previously noted that dmp is an excellent ligand for Cu(I) and will readily displace biq. Ligand **4**, which is sterically less well suited to Cu(I) than dmp, nevertheless is also quite effective at biq displacement.

Absorption and Luminescence Properties

As expected for an enantiomeric pair, the absorption and luminescence properties of Λ-Cu and Δ-Cu are identical. These properties are summarized in Table 1 along with those of $[Cu(phen)_2]^+$ and $[Cu(dmp)_2]^+$. Figure 2 shows the absorption and circular dichroism spectra of the complexes.

The absorption spectrum (CH_2Cl_2 solution, room temperature) shows very intense bands below 350 nm that can be assigned to LC transitions and a band in the visible region ($\lambda_{\max} = 442$ nm, $\epsilon_{\max} = 5700$ $M^{-1}cm^{-1}$) that is assigned to ^{1}MLCT transitions. It is known that the energy and intensity of the CT absorption band in Cu(I) phenanthroline systems is strongly influenced by the substituents on the ligands. Bulky groups in the 2,9-positions are thought to hinder the approach of the ligand to the metal ion, thereby limiting the development of CT intensity.[13] In fact, the intensity of the CT absorption band of Λ- and Δ-Cu is less intense than that of $[Cu(dmp)_2]^+$, but more intense than that of $[Cu(dpp)_2]^+$ (Table 1), as one could expect on the basis of the steric hindrance of the methyl, pinene, and phenyl substituents.

These complexes do not emit either in CH_2Cl_2 solution at 298 K or in CH_2Cl_2 rigid matrix at 77 K when excited in the visible region. This behavior is identical to that of $[Cu(phen)_2]^+$. The luminescence properties, as well as the absorption ones, of Cu(I) bis-phenanthroline complexes are influenced by the presence of substituents in the 2, 9-positions of phenanthroline. When phen ligands bear bulky groups in the 2,9-positions, the luminescence quantum yield and lifetime increase in solution, since these substituents shield the copper ion and prevent quenching by the solvent. This effect is evident in methanol but is also observed even in a weakly basic solvent like CH_2Cl_2. The correlation between the size of the 2,9-substituents and the luminescence lifetime does not hold in a rigid matrix at 77 K, where solvent quenching should be inhibited. The Λ- and Δ-Cu complexes have phen ligands substituted only on one side, leaving the other side open to intrusion by solvent. This metal shielding could explain why the luminescence properties of Δ- and Λ-Cu are more similar to those of $[Cu(phen)_2]^+$, but different from those of the 2,9-disubstituted phen complexes $[Cu(dmp)_2]^+$ and $[Cu(dpp)_2]^+$, which emit both at 298 and at 77 K. Moreover, the presence of the fused pinene substituent could induce an interligand repulsion causing a distortion from tetrahedral geometry, although from simple molecular modeling (HyperChem 2.0), this distortion does not seem to be evident. On the basis only of structural considerations, the lack of emission, even at 77 K, is difficult to explain for Δ- and Λ-Cu as well as for $[Cu(phen)_2]^+$.

Quenching Studies

An important reason for studying resolved complexes such as Δ- and Λ-Cu involves the question of stereoselectivity in electron[14] or energy[15] transfer. In several cases it has been found that the quenching process is highly stereoselective, leading to large differences in the k_q for the two enantiomers (up to 15: 1[14e]). Two complementary quenching studies were carried out in hopes of detecting such an effect.

The first experiment involved the determination of a Stern−Volmer quenching constant which, by the usual kinetic treatment, can be defined as $k_q = (\tau^{\circ}/\tau - 1/[Q]^{\circ})$ where $[Q]^{\circ}$ is the formal added quencher concentration. Stern−Volmer experiments were carried out using optically pure Δ- and Λ-$[Ru(bpy)_3]^{2+}$ as donors and Δ- and Λ-Cu as acceptors (CH_2Cl_2 air-equilibrated solution, 298 K; the ionic strength was controlled by adding tetrabutylammonium perchlorate, 52 mM). Four types of encounter complexes are possible: (1) Δ-Ru/Λ-Cu, (2) Δ-Ru/Δ-Cu, (3) Λ-Ru/Λ-Cu, (4) Λ-Ru/Δ-Cu. Among them, systems 1 and 4 and systems 2 and 3 are enantiomeric pairs; thus, they are expected to give the same results. In other words, systems 1 and 2 can be used to cross check the behavior of systems 4 and 3, respectively. In all cases, regardless of the chirality of the partners, the k_q values were 2.5×10^8 M^{-1} s^{-1}, within experimental error (20%).

The experiment described above, namely, the determination of the Stern−Volmer behavior for the Δ-donor/Δ-quencher and Λ-donor/Δ-quencher pairs, requires that both the donor and the acceptor are optically resolved. It is possible, however, to evidence the occurrence of a chiral quenching process even if the donor is racemic. In principle, for a solution containing the *rac*-donor and the Δ-quencher, two quenching processes (Δ-donor/Δ-quencher and Λ-donor/Δ-quencher) are possible.

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If $k_q^{\Delta\Delta}$ and $k_q^{\Lambda\Delta}$ are different, the decay of the *rac*-donor luminescence should be biexponential,[15d] with lifetimes $\tau_\Delta = 1/(k_d + k_q^{\Delta\Delta}[Q]°)$ and $\tau_\Lambda = 1/(k_d + k_q^{\Lambda\Delta}[Q]°)$ (k_d is the intrinsic excited-state decay constant of the donor complex). Thus, by means of a single luminescence decay measurement on a solution containing the racemic donor and a suitable amount of resolved quencher, it is possible to qualitatively see whether chiral quenching takes place, just by comparing the monoexponential vs biexponential fit of the donor luminescence decay. It is difficult to evaluate these considerations on a quantitative level since τ_Δ and τ_Λ must be considerably different in order to obtain a significant biexponential fit; however, this method can be useful as a preliminary indicator since it can be sensitive to differences between the two decay constants of only 10%.[15d]

The quenching behavior of the chiral but unresolved *rac*-$[Ru(dpb)_3]^{2+}$ complex (where dpb is 4,4′-diphenyl-2,2′-bipyridine) by the chiral *and* resolved Cu(I) complexes was explored. The luminescence decay of $[Ru(dpb)_3]^{2+}$ is monoexponential in air-equilibrated CH_2Cl_2 solution at 298 K and exhibits an excited-state lifetime of 535 ns under our experimental conditions. Addition of either chiral Cu quencher shortened the lifetime of this excited state, but its decay remained perfectly monoexponential. A k_q of 1.6×10^8 M^{-1} s^{-1} was estimated from the single-lifetime measurements.

These experiments indicate that there are no overriding geometric factors which limit the quenching efficiency of our systems. That there is no difference in the quenching constants for an enantiomeric pair of complexes such as $[Ru(bpy)_3]^{2+}$ is less surprising since these complexes are approximately spherical and a geometrically governed preference for Δ- or Λ-Cu appears unlikely. It is more surprising, however, that the substitution of bpy by the more extended ligand dpb does not evidence any substantial enantioselectivity, and, in fact, the quenching rate constants measured for $[Ru(bpy)_3]^{2+}$ and $[Ru(dpb)_3]^{2+}$ are quite similar. A possible explanation for these systems might be that electron or energy transfer quenching occurs through a distance over which chiral recognition leading to a more favorable collision interaction is not significant. Thus, to a quencher, even chiral, excited donors look virtually identical.

Future studies will examine the use of **4** and **6** as chiral auxiliaries in metal-catalyzed reactions and look for chiral induction in the formation of related metal complexes.

Experimental Section

Absolute EtOH, CH_2Cl_2 (Merck Uvasol), and tetrabutylammonium perchlorate (TBAP, Fluka) were used without further purification. The CH_3CN was refluxed overnight with CaH_2 and then distilled under Ar. (1*R*)-(+)-α-Pinene (97% ee), (1*R*)-(+)-*β*-pinene (97% ee), and (1*R*,5*S*)-(+)-nopinone (98% ee) were purchased from Aldrich. The 8-amino-7-quinolinecarbaldehyde[5] and $[Cu(CH_3CN)_4](ClO_4)$[16] were synthesized by following previously reported procedures. Resolved Δ- and Λ-$[Ru(bpy)_3](PF_6)_2$ were kindly supplied by Prof. Alex von Zelewsky,[17] whereas $[Ru(dpb)_3](PF_6)_2$ was prepared according to a literature procedure.[18] Melting points were obtained on a Hoover capillary melting point apparatus and were uncorrected. Optical rotations were measured on a Perkin-Elmer 141 polarimeter. Elemental analyses were performed by National Chemical Consulting, Tenafly, NJ. Cyclic voltammograms were recorded on a BAS CV-27 voltammograph and a Houston Instruments model 100 X-Y recorder according to a previously described procedure.[19]

HPLC separations were performed on a Waters 501 system. A *β*-cyclodextrin (Cyclobond I) ASTEC column (25 cm) was used for analysis of the chiral phen ligands. The eluent was 84:15:1 CH_3CN/MeOH/buffer. The buffer was prepared by adding 10% aqueous HOAc to a 1 mM aqueous triethylamine (TEA) solution to obtain pH 4. All solvents were filtered prior to use, and a flow rate of 0.6 mL/min was used. Peaks were monitored by their absorbance at $\lambda = 254$ nm.

(1*R*,5*S*)-(+)-(2,3-*b*)-Pineno-1,10-phenanthroline (4). To a solution of (1*R*,5*S*)-(+)-nopinone (**2**, 50 mg, 0.36 mmol) and 8-amino-7-quinolinecarbaldehyde (**3**, 62 mg, 0.36 mmol) in absolute EtOH (5 mL) was added saturated ethanolic KOH (0.5 mL). The solution was refluxed under Ar for 17 h. The solvent was evaporated, and the residue was redissolved in CH_2Cl_2 (10 mL) and then washed with H_2O (10 mL) to remove excess KOH. Concentration under reduced pressure, followed by column chromatography on alumina (20 g) eluting with diethyl ether gave a light yellow solid (**4**, 40 mg, 40%), mp 168−170 °C: ^1H NMR ($CDCl_3$) δ 9.20 (d, 1H, $J = 3.0$ Hz, H_9), 8.27 (d, 1H, $J = 6.6$ Hz, H_7), 7.95 (s, 1H, H_4), 7.73 (AB quartet, 2H, H_5/H_6), 7.60 (m, 1H, H_8), 3.63 (t, 1H, $J = 5.4$ Hz), 3.18 (d, 2H, $J = 2.0$ Hz), 2.83 (m, 1H), 2.41 (m, 1H), 2.15 (bs, H_2O), 1.46 (s, 3H, CH_3), 1.38 (d, 1H, $J = 9.9$ Hz), 0.70 (s, 3H, CH_3); ^{13}C NMR δ 167.8, 149.7, 149.5, 145.2, 142.2, 136.4, 134.3, 131.4, 128.1, 127.8, 126.5, 124.9, 122.2, 51.0, 39.8, 39.3, 31.4, 30.7, 25.9, 21.3. Anal. Calcd for $C_{19}H_{18}N_2 \cdot 0.25H_2O$: C, 81.87; H, 6.60; N, 10.05. Found: C, 82.36; H, 6.56; N, 10.13.

(1*S*,5*R*)-(−)-(2,3-*b*)-Pineno-1,10-phenanthroline (6). Following the above procedure for **4**, (1*S*,5*R*)-(−)-nopinone (200 mg, 1.45 mmol) and **3** (249 mg, 1.45 mmol) in absolute EtOH (8 mL) yielded 230 mg (58%) of a light yellow solid, mp 168−170 °C: ^1H NMR ($CDCl_3$) δ 9.21 (d, 1H, $J = 3.0$ Hz, H_9), 8.27 (d, 1H, $J = 6.6$ Hz, H_7), 7.95 (s, 1H, H_4), 7.73 (AB quartet, 2H, H_5/H_6), 7.60 (m, 1H, H_8), 3.63 (t, 1H, $J = 5.4$ Hz), 3.17 (d, 2H, $J = 2.0$ Hz), 2.82 (m, 1H), 2.40 (m, 1H), 1.45 (s, 3H, CH_3), 1.38 (d, 1H, $J = 9.9$ Hz), 0.70 (s, 3H, CH_3); ^{13}C NMR δ 167.7, 149.7, 149.6, 145.4, 142.4, 136.1, 134.1, 131.2, 128.1, 127.7, 126.3, 124.9, 122.1, 51.0, 39.7, 39.2, 31.3, 30.6, 25.8, 21.3.

[Cu(4)$_2$]ClO$_4$. To a solution of (1*R*,5*S*)-(+)-(2,3-*b*)-pineno-1,10-phenanthroline (**4**, 20 mg, 0.073 mmol) in CH_3CN (7 mL) was added solid $[Cu(CH_3CN)_4]ClO_4$ (12 mg, 0.036 mmol). The dark red solution was stirred at room temperature for 10 min. Concentration of the solution under vacuum gave 25 mg (96%) of [Cu(**4**)$_2$]ClO$_4$ as air-stable deep red crystals: ^1H NMR (CD_3CN) δ 8.79 (d, 2H, $J = 4.2$ Hz), 8.60 (d, 2H, $J = 7.2$ Hz), 8.35 (s, 2H), 8.06 (AB quartet, 4H, H_5/H_6), 7.79 (quartet, 2H, H_8), 3.23 (bs, 4H, $-CH_2-$), 2.80 (t, 2H, $-CH_2-$), 2.44 (m, 2H, $-CH_2-$), 2.29 (m, 2H, $-CH_2-$), 2.18 (bs, H_2O), 1.20 (d, 2H, $J = 9.9$ Hz), 0.91 (s, 6H, CH_3), 0.52 (s, 6H, CH_3); MS (*m*/*e*) 611 $(M - ClO_4)^+$. Anal. Calcd for $C_{38}H_{36}N_4CuClO_4$: C, 64.14; H, 5.06; N, 7.88. Found: C, 64.21; H, 4.80; N, 7.53. ***CAUTION!*** *Perchlorate salts are potentially explosive!*

[Cu(6)$_2$]ClO$_4$. Following the procedure for [Cu(**4**)$_2$]ClO$_4$, (1*S*,5*R*)-(−)-(2,3-*b*)-pineno-1,10-phenanthroline (**6**, 80 mg, 0.30 mmol) was treated with $[Cu(CH_3CN)_4]ClO_4$ (48 mg, 0.15 mmol) in CH_3CN (10 mL) to give 100 mg (93%) of [Cu(**6**)$_2$]ClO$_4$ as air-stable deep red crystals: ^1H NMR (CD_3CN) δ 8.79 (d, 2H, $J = 4.2$ Hz), 8.60 (d, 2H, $J = 7.2$ Hz), 8.35 (s, 2H), 8.06 (AB quartet, 4H, H_5/H_6), 7.79 (quartet, 2H, H_8), 3.23 (bs, 4H, $-CH_2-$), 2.80 (t, 2H, $-CH_2-$), 2.44 (m, 2H, $-CH_2-$), 2.29 (m, 2H, $-CH_2-$), 2.18 (bs, H_2O), 1.20 (d, 2H, $J = 9.9$ Hz), 0.91 (s, 6H, CH_3), 0.52 (s, 6H, CH_3); MS (*m*/*e*) 611 $(M - ClO_4)^+$. ***CAUTION!*** *Perchlorate salts are potentially explosive!*

Spectroscopy. NMR spectra were recorded on a General Electric QE-300 spectrometer at 300 MHz for ^1H and 75 MHz for ^{13}C. Chemical shifts are reported in parts per million downfield from internal TMS with solvent peaks as reference. Infrared spectra were recorded on an ATI Mattson Genesis Series FT-IR interfaced to a Dell PC. Absorption and emission spectra were recorded with a Perkin-Elmer Lambda-6 spectrophotometer and a Perkin-Elmer LS-50 spectrofluorimeter, respectively. Emission spectra at 298 K were performed in air-equilibrated CH_2Cl_2 solution; emission spectra in CH_2Cl_2 rigid matrix

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were recorded at 77 K using glass tubes immersed in a glass dewar filled with liquid nitrogen. Circular dichroism spectra were recorded with a Jasco J-710 spectropolarimeter. Luminescence lifetimes were measured with an Edinburgh single-photon counting apparatus (N_2 lamp, $\lambda_{ex} = 337$ nm). The monitored emission band was isolated by means of cutoff filters. Experimental errors: absorption and emission maxima, ±2 nm; molar extinction coefficients and excited-state lifetimes, ±10%.

Quenching Studies. All experiments were performed in CH_2Cl_2 with 0.05 M tetrabutylammonium perchlorate (TBAP) as ionic strength buffer. The concentration of the Ru(II) complexes used as luminophores was 5×10^{-4} M, whereas the concentrations of the Cu(I) complexes used as quenchers were in the range 10^{-2}–10^{-3} M. The luminescence quenching of the Ru(II) complexes was evaluated by lifetime measurements where the luminescence decay was followed for 5 half-lives; quantitative luminescence intensity measurements were not possible because of the very large absorbance of the solution. For the same reason, luminescence lifetime measurements were performed using triangular quartz cells with 45° excitation in order to limit inner filter effects. The Stern–Volmer plots were linear, and the quenching rate constants were calculated from the slope of such plots using a least-squares fitting. The error on the quenching rate constants was estimated to be 20%.

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