Chiroptical Properties of an Optically Pure Dicopper(I) Trefoil Knot and Its Enantioselectivity in Luminescence Quenching Reactions

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Abstract: Chiroptical spectroscopy is used to investigate the properties of an optically pure dinuclear copper(I) trefoil knot. For the metal-to-ligand charge tranfer (MLCT) transition in the visible region (520 nm), the electric and magnetic transition dipole moments are determined from absorption and circular dichroism spectra: 2.8 Debye and 0.5 Bohr magneton (μ_B). Circular polarization in the luminescence (CPL) of the knot is determined and this allows the electric and magnetic transition dipole moments in emission to be calculated: 0.02 Debye and 0.003 μ_B. The large difference between the moments in absorption and emission shows that the emission observed does not originate directly from the ^{1}MLCT state. Given the low probability for radiative decay we assign the long-lived emitting excited state to a ^{3}MLCT state. The copper(I) trefoil knot is found to quench the emission from Tb^{III} and $Eu^{III}(dpa)_3^{3-}$ (dpa = pyridine-2,6-dicarboxylate) with a bimolecular rate constant of 3.2 and $3.3 \times 10^7 M^{-1} s^{-1}$, respectively, at room temperature in water–acetonitrile (1:1 by volume). Experimental results indicate that the (Λ)-knot preferentially quenches the Λ enantiomer of the lanthanide complex with an enantioselectivity (ratio of quenching rate constants for Δ and Λ: kq^{Λ}/kq^{Δ}) of 1.012 ± 0.002 for Eu^{III} and 1.018 ± 0.003 for Tb^{III}.

Keywords: chirality · circular dichroism · lanthanides · luminescence · supramolecular chemistry · trefoil knot

Introduction

A trefoil knot is a fascinating chiral object since it is topologically chiral. Contrary to Euclidian chirality,[1] which is described by distances and angles, topological chirality is a higher level of description and implies that the molecular graph of a topologically chiral object is nonplanar.[2] Made of a single knotted closed ring, the trefoil knot, which requires a minimum of three crossing points for its representation in a two-dimensional space, is an unconditionally topologically chiral object[2–3] and its two topological enantiomers are represented in Figure 1. It should be noted that two topological enantiomers can not be interconverted by continuous deformation, therefore totally excluding racemization as long as no bond in their organic backbone is broken.

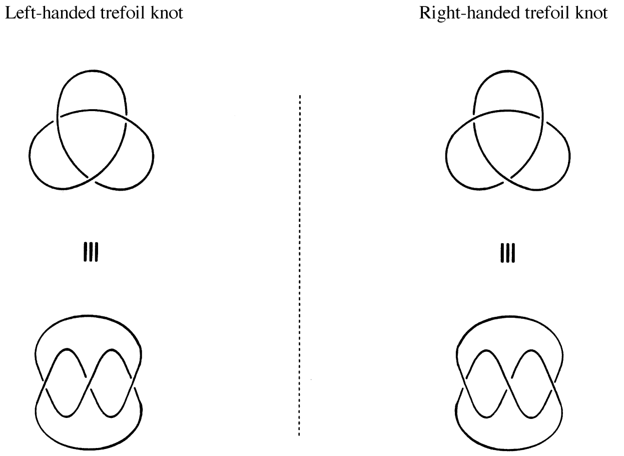

Figure 1. The two topological enantiomers of a trefoil knot. The top and bottom representations are obviously very different but they correspond to topologically identical objects (isotopic species).

The first theoretical discussion on molecular trefoil knots appeared in the chemical literature in 1961.[4] At that time, knots were considered as exotic and highly hypothetical species. Nevertheless, the trefoil knot has exerted a real fascination on several research groups,[5] sometimes in relation with chirality. In this context, an interesting discussion on the putative chiroptical properties of the theoretical trefoil

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0947-6539/00/0612-2129 $ 17.50+.50/0

knot consisting of 66 methylene groups was published long ago, in which a very small rotation was predicted for simple hydrocarbon knots.[6]

The introduction of template strategies for making catenanes (interlocking ring systems) and knots turned out to be determining.[7] The first report on the synthesis of a trefoil knot using synthetic chemistry[8] was followed by the description of single-stranded DNA displaying knotted topologies.[9] Very recently, aromatic donor–acceptor complexes have also been used as precursors to knotted cycles.[10]

Since the first reported synthesis of a trefoil knot,[8] significant synthetic improvements have allowed their gram-scale preparation.[11] The dicopper(I) trefoil knot presented in Figure 2 had been resolved earlier[12] by the formation of diastereomers. To this end, an optically pure anion, 1,1′-binaphthyl-2,2′-diylphosphate, was associated to the dicopper(I) knot ((+)-**K** $\cdot$ 2Cu $\cdot$ 2PF_6) and the two diastereomers formed were separated by diastereoselective crystallization. The chiral auxiliary was easily replaced by PF_6^- in order to obtain the pure enantiomers.

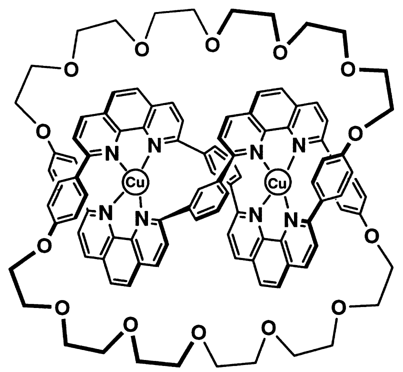

Figure 2. The dicopper(I) trefoil knot used in this study: (+)-**K** $\cdot$ 2Cu $\cdot$ 2PF_6.

Abstract in French: *Les propriétés chiroptiques d'un nœud optiquement pur de cuivre(I) ont été étudiées par spectroscopies. Pour la transition de transfert de charge du métal vers le ligand dans le visible (520 nm), les moments dipolaires électriques et magnétiques de transition sont déterminés à partir des spectres d'absorption et de dichroïsme circulaire: 2,8 Debye et 0,5 magnéton de Bohr (μ_B) respectivement. La polarisation circulaire de l'émission mesurée sur le nœud a d'autre part permis de déterminer les moments dipolaires électrique et magnétique de transition en émission: 0,02 Debye et 0,003 μ_B respectivement. La différence importante entre les moments dipolaires en absorption et en émission montre que l'émission observée ne provient pas directement de l'état ^{1}MLCT. Etant donnée la faible probabilité de la décroissance de l'émission, l'état excité émetteur a été attribué à un état ^{3}MLCT. Dans une seconde partie, il a été montré que le nœud de cuivre(I) piège l'émission des complexes de Tb^{III} et $Eu^{III}(dpa)_3^{3-}$ (dpa = pyridine-2,6-dicarboxylate) avec une constante bimoléculaire de piégeage de 3,2 et 3,3 × 10^7 $M^{-1}s^{-1}$ respectivement, à température ambiante dans un mélange eau-acétonitrile (1:1 en volume). Les résultats indiquent que le nœud de configuration absolue Λ piège préférentiellement l'émission de l'énantiomère Λ du complexe de lanthanide avec une énantiosélectivité (ratio des constantes de vitesse de piégeage pour Δ et Λ: kq^{Λ}/kq^{Δ}) de 1,012 ± 0,002 pour Eu^{III} et 1,018 ± 0,003 pour Tb^{III}.*

In the present study we report the chiroptical properties of the dicopper(I) trefoil knot. For this compound, the topological chirality is associated with helicity in the central copper(I) bisphenanthroline core of the molecule resulting in circular dichroism (CD) of the metal-to-ligand charge transfer (MLCT) electronic transitions. The chirality of the molecule in the excited state is reflected by a difference in intensity of the left and right circularly polarized components of luminescence light.

An interesting property of molecules with topological chirality[13] is that racemization, which for these compounds requires the breaking and reforming of a covalent bond, can be excluded under nondestructive conditions. This makes topologically chiral molecules interesting as potential enantioselective catalysts or auxiliary reagents in chemical reactions. Furthermore, the thermal and photochemical stability of the dicopper(I) knot makes it a potentially useful enantioselective energy quencher.[14] In the second part of this study we investigate the behavior of (+)-**K** $\cdot$ 2Cu $\cdot$ 2PF_6 in this respect.

In the last decade a large number of studies have been devoted to enantioselectivity in quenching of the luminescence of chiral lanthanide complexes by chiral, resolved transition metal complexes and bioinorganic compounds.[15] It has been shown that small alterations in the structure of the quencher molecule (e.g. the replacement of a hydrogen atom capable of forming a hydrogen bond by a methyl group) can have a large effect on the chiral discrimination.[15] In a first attempt to characterize the chirality of the copper(I) knot by the enantioselectivity displayed in interactions with other chiral molecules, we investigated the enantioselective quenching of terbium(III) and europium(III) tris(dpa) (dpa = pyridine-2,6-dicarboxylate) luminescence.

Results and Discussion

Circular polarization in absorption and emission: The absorption spectrum of **K** $\cdot$ 2Cu $\cdot$ 2PF_6 is depicted in Figure 3. Circular dichroism spectra of both enantiomers are shown in Figure 4.

In the absorption spectrum of the knot a band of moderate intensity in the visible range of the spectrum can be observed. This band, which also occurs in $Cu(phen)_2^+$ complexes, has been assigned to an MLCT transition. Interestingly the transition is also circular dichroic (Figure 4). The dissymmetry ratio ($g_{abs} = \Delta\varepsilon/\varepsilon$) is practically constant over the entire visible band. This is a good indication that the broad band including a shoulder at about 590 nm derives its oscillator strength from a single electronic transition. By fitting to gaussian curves the experimental absorption spectrum in the range from 480 to 800 nm and numerical integration area under the fitted curves, we found using Equation (1) (see Methods in the

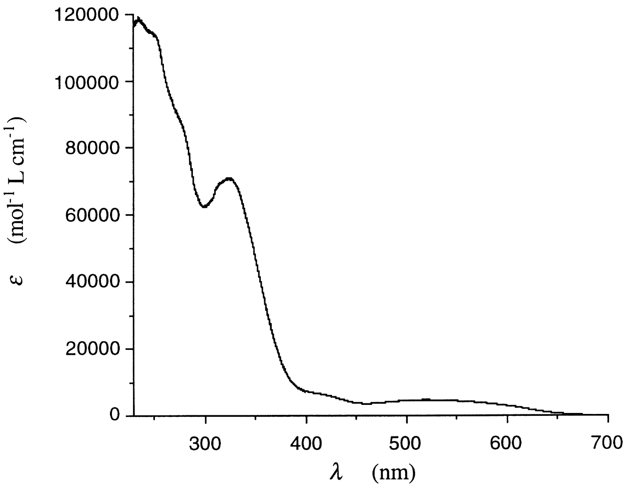

Figure 3. UV/Vis spectrum of $\mathbf{K}\cdot 2\,Cu\cdot 2\,PF_6$ (8.7×10^{-6} M in CH_2Cl_2).

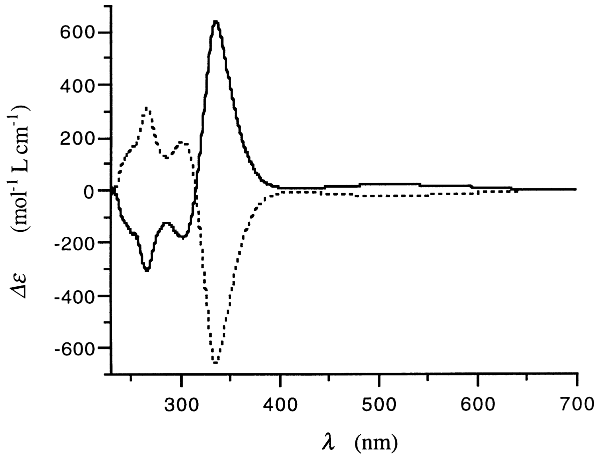

Figure 4. CD spectra (CH_2Cl_2) of (+)-$\mathbf{K}\cdot 2\,Cu\cdot 2\,PF_6$ (continuous line) and (−)-$\mathbf{K}\cdot 2\,Cu\cdot 2\,PF_6$ (dashed line).

Experimental Section) an electric transition dipole moment of $\mu = 2.8$ Debye.

From X-ray diffration on crystals of the knot it is known that the symmetry of the knot is D_2.[12] In this symmetry group electric and magnetic transition dipole moments are always parallel ($\Theta_{if} = 0$). Taking $g_{abs} = 0.007$ we obtain, using Equation (2), the magnetic dipole moment of the transition: $m = 0.5\,\mu_B$. Matrix elements of the magnetic dipole moment operator $\hat{\mathbf{m}} = \frac{\mu_B}{\hbar}(\hat{\mathbf{L}} + g\hat{\mathbf{S}})$ contain an orbital (**L**) and a spin (**S**) part but in practice only transitions with $\Delta S = 0$ contribute significantly. For transitions involving d orbitals the contribution from the L operator is limited to about $2\,\mu_B$. Since the experimental magnetic moment is close to this theoretical limit we conclude that the visible transition is almost fully magnetic-dipole allowed.

This result is surprising since in previous reports on spectroscopic properties of D_{2d}-symmetric $Cu(phen)_2^+$ complexes, a long wavelength shoulder (near 550 nm) and the main band (480 nm) were distinguished and interpreted as arising from different electronic transitions ($^1A_2$ and $^1B_2$ in D_{2d} symmetry).[16] The linear polarization of these two bands was found to be along the same direction, and a lowering of the symmetry of the chromophore from D_{2d} to D_2 was proposed to account for the intensity of the formally electric-dipole forbidden (but magnetic dipole allowed) $^1A_1 - {}^1A_2$ transition: the two transitions are now characterized by the same irreducible representation ($^1B_2$). For chiral Cu^I bisphenanthroline complexes, CD of opposite sign is observed for the main MLCT band and the long wavelength shoulder.[17] In the absorption spectrum of the knot a long wavelength shoulder can also be distinguished (ca. 590 nm). With CD spectroscopy, which is also sensitive towards magnetic dipole transitions, it is not possible to distinguish more than one electronic transition.

As reported previously,[18] $\mathbf{K}\cdot 2\,Cu\cdot 2\,PF_6$ also shows luminescence which was assigned to an MLCT transition (Figure 5). We found the luminescence from the enantiopure knot to be circularly polarized, the degree of circular polarization of the luminescence (g_{lum}) being practically constant and of the same order of magnitude as g_{abs} (Tables 1 and 2).

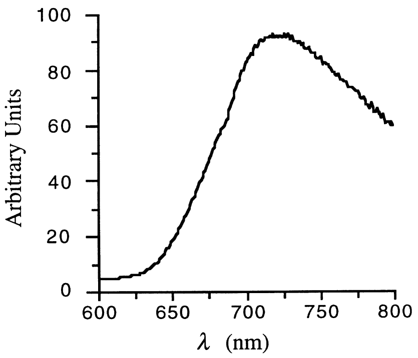

Figure 5. Luminescence spectrum of $\mathbf{K}\cdot 2\,Cu\cdot 2\,PF_6$ (excitation: 520 nm, $\tau_o = 200$ ns, $\Phi = 9\times10^{-4}$).

Table 1. Location and properties of the bands observed in the CD spectrum of (+)-$\mathbf{K}\cdot 2\,Cu\cdot 2\,PF_6$ and (−)-$\mathbf{K}\cdot 2\,Cu\cdot 2\,PF_6$.

CD spectra type	Features wavelength [nm]		Δε [M^{-1}cm^{-1}]		ε [M^{-1}cm^{-1}]	$g_{abs}\times10^3$	
	(+)-**K**	(−)-**K**	(+)-**K**	(−)-**K**	(+)- or (−)-**K**	(+)-**K**	(−)-**K**
shoulder	244	245	−154	+155	115105	−1.34	+1.35
extremum	266	267	−306	+306	96243	−3.18	+3.18
extremum	302	302	−180	+179	62600	−2.88	+2.86
extremum	336	335	+640	−640	64792	9.88	−9.88
extremum	508	507	+20.8	−20.7	2945	7.06	−7.03

Table 2. Absorption and emission dissymmetry factors measured at the maximum and on both sides of the MLCT band for (+)-$\mathbf{K}\cdot 2\,Cu\cdot 2\,PF_6$ and (−)-$\mathbf{K}\cdot 2\,Cu\cdot 2\,PF_6$ (all experiments were performed at 20 °C in CH_2Cl_2).

		λ [nm]		
Emission		680	720	760
g_{lum} (× 10^3)	(+)-$\mathbf{K}\cdot 2\,Cu\cdot 2\,PF_6$	4.4	5.1	4.4
	(−)-$\mathbf{K}\cdot 2\,Cu\cdot 2\,PF_6$	−4.5	−5.2	−4.4
Absorption		470	510	550
g_{abs} (× 10^3)	(+)-$\mathbf{K}\cdot 2\,Cu\cdot 2\,PF_6$	7.1	7.1	6.5
	(−)-$\mathbf{K}\cdot 2\,Cu\cdot 2\,PF_6$	−7.0	−7.0	−6.3

From the reported emission lifetime (200 ns) and quantum yield (9×10^{-4}) of the luminescence a radiative lifetime of 0.2 ms is derived,[18] and from this number we calculate an electric transition dipole moment of about 0.02 Debye and a magnetic moment of 0.003 μ_B. These numbers are more than an order of magnitude smaller than those determined from absorption and circular dichroism data. Therefore it seems highly unlikely that the long-lived excited state is the ^{1}MLCT. Given its long radiative lifetime it has to be assigned to a triplet state.

In a first approximation, the lowest triplet state (T_1) is expected to be based on the same orbital configuration as the lowest excited singlet state (S_1). In D_2 symmetry however this triplet state will not contain a sublevel of the same symmetry as the S_1 state and hence the $T_1 - S_0$ transition cannot 'borrow' intensity from the $S_0 - S_1$ transition since mixing of T_1 and S_1 is forbidden by symmetry. Still the values for g_{abs} and g_{lum} are very similar. A possible explanation for the observed chiroptical effect in emission is that the lowest triplet state borrows its intensity from a higher excited state. Looking at Table 1 the state associated with the 336 nm absorption band is a likely candidate.

Another possible explanation, which is supported by previous measurements of the temperature dependence of the emission lifetime and bandshape of bis(4,4′,6,6′-tetramethyl-2,2′-bipyridine)Cu^I and bis (2,9-dimethyl-1,10-phenanthroline)Cu^I complexes,[16] is that the emission originates from the lowest excited singlet state which is populated by thermal excitation from the triplet state. This requires a small (<1000 cm^{-1}) energy difference between singlet and triplet state.

Enantioselectivity in luminescence quenching: To see whether the chirality of the knot also expresses itself in enantioselectivity in bimolecular reactions with a chiral reaction partner, we have investigated the energy transfer reaction between photoexcited lanthanide chelates (donor) and the knot (acceptor). Experiments with racemic **K**$\cdot 2\,Cu \cdot 2\,PF_6$ show that the compound is indeed able to quench the luminescence of $[Eu^{III}(dpa)_3]^{3-}$ and $[Tb^{III}(dpa)_3]^{3-}$ and we ascribed this quenching to energy transfer.

The decay constant of the lanthanide luminescence (reverse of the lifetime) depends linearly on the knot concentration (Figure 6), indicating a bimolecular reaction mechanism involving the formation of encounter complexes of photoexcited lanthanide chelate and knot by diffusional motion. The quenching rate constants have been determined (Table 3).

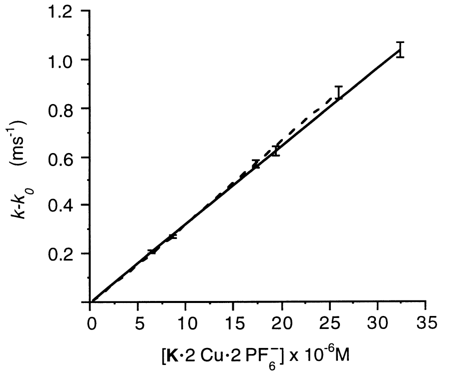

Figure 6. Quenching experiment of $[Tb(dpa)_3]^{3-}$ (continuous line) and $[Eu(dpa)_3]^{3-}$ (dashed line) by (+)-**K**$\cdot 2\,Cu \cdot 2\,PF_6$. For conditions, see Table 3.

Table 3. Stern–Volmer parameters for the quenching by (+)-**K**$\cdot 2\,Cu \cdot 2\,PF_6$ of $[Tb(dpa)_3]^{3-}$ (543 nm, 40 mM) and $[Eu(dpa)_3]^{3-}$ (615 nm, 40 mM) in MeCN–water (1:1).

	k_Q [M^{-1}s^{-1}]	Standard deviation
$[Tb(dpa)_3]^{3-}$	3.2×10^7	0.1×10^7
$[Eu(dpa)_3]^{3-}$	3.3×10^7	0.1×10^7

The mechanism of energy transfer from these lanthanide complexes is not very well known but there are contributions from the Förster mechanism (dipole–dipole mechanism, transfer at long distance) and the Dexter mechanism (transfer at short distance, requiring orbital overlap) in proportions which we cannot clearly quantify. Using the optically resolved knot (+)-**K**$\cdot 2\,Cu \cdot 2\,PF_6$ as quencher, we measured the circular polarization of the luminescence from $[Eu^{III}(dpa)_3]^{3-}$ (0.4 mM in a 1:1 (v/v) water–acetonitrile mixture) partially quenched by (+)-**K**$\cdot 2\,Cu \cdot 2\,PF_6$ (23 µM). The photophysical processes are detailed in Figure 7.

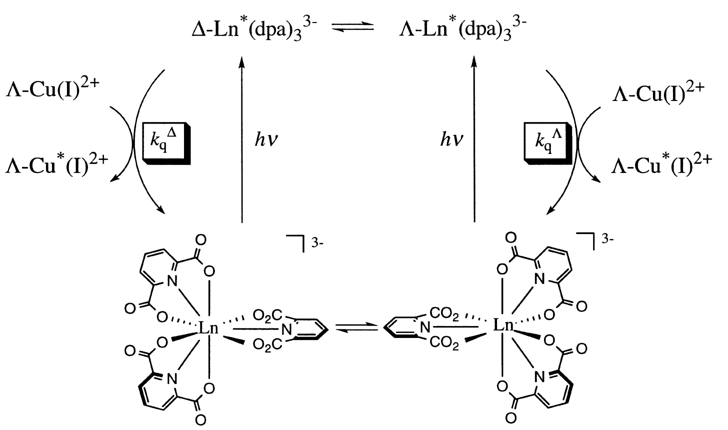

Figure 7. After irradiation of a racemic mixture of the Ln^{III} complex (Ln = Eu or Tb), the excited state is quenched by the optically pure dicopper(I) trefoil knot. The diastereomeric interactions between the Δ and Λ stereoisomers of the Ln^{III} complexes and the Λ stereoisomer of the quencher are responsible for the different rate constants. k_q^{Δ} and k_q^{Λ} being different, the emission of the lanthanide complex is now circularly polarized.

The degree of circular polarization amounts to: $g_{lum}^{cw} = -(1.3 \pm 0.2) \times 10^{-3}$ (wavelength of detection 595 nm, optical bandwidth 4 nm). In this measurement the optical pathlength of the Eu^{III} luminescence through the solution was kept small (<1 mm) in order to avoid artificial induction of circular polarization of the Eu luminescence by circular dichroic absorption of the resolved knot. Under these conditions the average decay constant of the Eu^{III} luminescence is 1.1 ms^{-1}. In the absence of quencher we found $k_o = 0.585$ ms^{-1}. From Equation (10), using $g_{lum}^{\Lambda} = +0.45$, we calculate $E_q = (-6 \pm 1) \times 10^{-3}$ which corresponds to a difference in the quenching rate constant of (1.2 ± 0.2) %.

For a sample solution of $[Tb^{III}(dpa)_3]^{3-}$ (0.4 mM) and (+)-**K**$\cdot 2\,Cu \cdot 2\,PF_6$ (37 µM, 1:1 (v/v) water–acetonitrile) we have measured $k_0 = 0.485$ ms^{-1}, $k^{av} = 1.565$ ms^{-1} and $g_{lum}^{cw} = (-1.2 \pm 0.2) \times 10^{-3}$ (543 nm, 2 nm bandwidth). With these values we found $E_q = (-9 \pm 2) \times 10^{-3}$ and consequently a difference in the quenching rate constant of (1.8 ± 0.3) %, which is com-

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parable to the amplitude measured with the europium complex. The sign of $g_{\mathrm{lum}}^{\mathrm{cw}}$ allowed us to assign the excess of emission to one enantiomer of the lanthanide complex. In the case of europium(III) and terbium(III), the sign of $g_{\mathrm{lum}}^{\mathrm{cw}}$ is negative which corresponds to an excess of luminescence of the Δ enantiomers. Therefore the Λ enantiomers are found to be preferentially quenched by the Λ enantiomer of the knot.

In summary, circular dichroism and circular polarization of the luminescence are presented for the resolved dicopper(I) trefoil knot. The observation of enantioselectivity in the quenching of chiral lanthanide chelates by the dicopper(I) trefoil knot indicates that the knot can exert chiral discrimination in bimolecular reactions. The dextrorotatory knot was found to quench preferentially the emission of the lanthanide complexes with Λ configuration. Therefore, the homochiral interaction (Λ-Λ) of the two actors (donor and acceptor) seems to be privileged against the heterochiral interaction (Λ-Δ). In terms of enantiomeric excess of luminescence we found 1.2 % in the case of the $\mathrm{Eu^{III}}$ complex and 1.8 % for the $\mathrm{Tb^{III}}$ compound. This low enantioselectivity could be attributed to the fact that energy quenching can occur without contact between the species (Förster long-distance mechanism). If the contribution of this mechanism is significant, no diastereomeric interactions are available to induce a difference in the quenching rate constants. Besides, if we consider the Dexter short-distance mechanism, non-recognition of the double-helix copper core of the knot by the triple-helical lanthanide complex could account for a weak interaction between the two partners, yielding again the observed low enantioselectivity. Further studies using triple helices as acceptors should clarify this point.

Experimental Section

Materials: Synthesis and resolution of the dicopper(I) trefoil knot have been reported earlier.[12] Lanthanide complexes were prepared by mixing aqueous solutions of ligand (Janssen Chimica) and lanthanide trischloride salt (Aldrich).

Measurements: CD spectra were recorded on a Jobin-Yvon CD6 dichrograph, absorption spectra on a Varian Cary 3 spectrometer. CPL and lanthanide emission lifetimes were recorded on a home-built instrument described earlier.[19]

Methods

Circular polarization in absorption and emission: Values for electric and magnetic dipole moments can be obtained from quantitative analysis of absorption and circular dichroism spectra using Equations (1) and (2).[20] According to Equation (1), integration of the molar decadic extinction coefficient over a particular absorption band yields the dipole strength (D) of the corresponding transition between states initial (i) and final (f), where μ is the electric dipole operator (in units of Debye) and n the refractive index of the solvent.

$$D_{\mathrm{if}} = |<i|\mu|f>|^2 = 92.0 \times 10^{-4}\,\frac{9n}{(n^2+2)^2}\int\frac{\varepsilon}{\nu}\mathrm{d}\nu \tag{1}$$

The circular dichroism depends on the relative magnitude and orientation of the electric and magnetic transition dipole moment. In the case where the dissymmetry ratio g_{abs} is constant throughout the absorption band, g_{abs} depends on the electric and magnetic transition dipole moments as given by Equation (2).[21]

$$g_{\mathrm{abs}} = \frac{\Delta\varepsilon}{\varepsilon} \cong 4\left(\frac{3n}{n^2+2}\right)\frac{R_{\mathrm{abs}}}{D_{\mathrm{abs}}} = 4\left(\frac{3n}{n^2+2}\right)\frac{(m_{\mathrm{fi}}/108)\cos(\Theta_{\mathrm{if}})}{\mu_{\mathrm{if}}} \tag{2}$$

Here n is the refractive index of the solvent, m_{fi} the magnetic transition dipole moment (in units of μ_{B}, the electronic Bohr magneton) and Θ_{if} the angle between the electric and magnetic transition dipole moment. The rotational strength (R) is obtained from integration of the circular dichroism over a particular band. For certain classes of molecular symmetry (e.g. groups C_{n} or D_{n}) however, electric and magnetic dipole moments of a particular transition are always parallel and for molecules belonging to these symmetry groups, the magnitude of electric and magnetic transition dipole moments can therefore be calculated from the absorption and CD spectra.

For emissive transitions, the value of the electric transition moment (μ'_{if}) can be calculated from the radiative lifetime and the emission band shape using the Strickler–Berg equation.[22] To obtain values for the magnetic transition dipole moment (m'_{if}) one has to resort to CPL measurements. The degree of circular polarization in emission is defined by Equation (3), where I_{L} (I_{R}) denotes the intensity of left (right) circularly polarized light.

$$g_{\mathrm{lum}} = \frac{2(I_{\mathrm{L}}-I_{\mathrm{R}})}{(I_{\mathrm{L}}+I_{\mathrm{R}})} \cong 4\left(\frac{3n}{n^2+2}\right)\frac{R_{\mathrm{lum}}}{D_{\mathrm{lum}}} = 4\left(\frac{3n}{n^2+2}\right)\frac{(m'_{\mathrm{fi}}/108)\cos(\Theta'_{\mathrm{if}})}{\mu'_{\mathrm{if}}} \tag{3}$$

When the electric moment in emission μ'_{if} is known from combined emission lifetime and quantum efficiency measurements, the magnetic dipole moment in emission (m'_{if}) may be calculated from g_{lum} measurements.

If the nuclear geometry of the molecule in the excited state is not distorted with respect to the ground state geometry, one expects the values for electric and magnetic transition dipole moments and the degree of circular polarization to be the same for the absorptive and emissive transition.

Enantioselectivity in luminescence quenching: Enantiomerically resolved chiral molecules with low-lying excited states can act as enantioselective quenchers of the luminescence from racemic tris chelates. Well studied is the quenching of Eu and $[\mathrm{Tb(dpa)_3}]^{3-}$ by $\mathrm{Co^{III}}$ tris-cyclohexane-1,2-diamine complexes[23] and $\mathrm{Ru^{II}}$ tris-1,10-phenanthroline.[24] In these experiments a small quantity of quencher was added to a racemic solution of the lanthanide complex. The quenching reactions may be written according to Equations (4) and (5), where Ln stands for the lanthanide complex with its chirality (Δ or Λ) and Q stands for the chiral quencher. Species in an electronically excited state are labelled with an asterisk. In Equations (4) and (5), $k_{\mathrm{q}}{}^{\Delta}$ and $k_{\mathrm{q}}{}^{\Lambda}$ denote the quenching rate constants for the lanthanide enantiomers with Δ and Λ chirality, respectively.

$$(\Delta)\text{-Ln*}+\mathrm{Q} \overset{k_{\mathrm{q}}^{\Delta}}{\rightleftharpoons} (\Delta)\text{-Ln}+\mathrm{Q*} \tag{4}$$

$$(\Lambda)\text{-Ln*}+\mathrm{Q} \overset{k_{\mathrm{q}}^{\Lambda}}{\rightleftharpoons} (\Lambda)\text{-Ln}+\mathrm{Q*} \tag{5}$$

The excited state population of a single Ln enantiomer, Ln*, is expected to decay strictly exponentially ($\approx\exp(-k\mathrm{t})$) with a decay constant given by Equation (6) and (7), where k_{o} is the decay constant in the absence of quencher.

$$k^{\Delta} = k_{\mathrm{o}} + k_{\mathrm{q}}{}^{\Delta}[\mathrm{Q}] \tag{6}$$

$$k^{\Lambda} = k_{\mathrm{o}} + k_{\mathrm{q}}{}^{\Lambda}[\mathrm{Q}] \tag{7}$$

By symmetry considerations k_{o} is the same for both enantiomers. In the presence of Q, the quenching rate constants $k_{\mathrm{q}}{}^{\Lambda}$ and $k_{\mathrm{q}}{}^{\Delta}$ may be different corresponding to different lifetimes of Λ-Ln* and Δ-Ln*. The enantioselectivity in the quenching is usually expressed by Equation (8); the parameter E_{q} varies between -1 and $+1$, where the boundary values apply when the reaction is completely enantioselective.

$$E_{\mathrm{q}} = (k_{\mathrm{q}}{}^{\Delta} - k_{\mathrm{q}}{}^{\Lambda})/(k_{\mathrm{q}}{}^{\Delta} + k_{\mathrm{q}}{}^{\Lambda}) \tag{8}$$

For very small levels of enantioselectivity in the quenching, measurement of g_{lum} in a continuous-wave (cw) fashion provides a sensitive method to detect enantioselectivity in the quenching; Equation (9) describes this phenomenon, and can be rewritten as Equation (10).

$$g_{\mathrm{lum}}^{\mathrm{cw}}(\lambda) = g_{\mathrm{lum}}^{\Lambda}(\lambda)(k_{\mathrm{q}}{}^{\Delta} - k_{\mathrm{q}}{}^{\Lambda})[\mathrm{Q}]/(2k_{\mathrm{o}} + (k_{\mathrm{q}}{}^{\Delta} + k_{\mathrm{q}}{}^{\Lambda})[\mathrm{Q}]) \tag{9}$$

$$g_{\mathrm{lum}}^{\mathrm{cw}}(\lambda) = E_{\mathrm{q}}{}_{\mathrm{lum}}^{\Lambda}(\lambda)(k^{\Delta} + k^{\Lambda})/(k^{\Delta} + k^{\Lambda} - 2k_{\mathrm{o}}) = E_{\mathrm{q}}g_{\mathrm{lum}}^{\Lambda}(\lambda)(k^{\mathrm{av}})/(k^{\mathrm{av}} - k_{\mathrm{o}}) \tag{10}$$

Here the parameter $g_{\mathrm{lum}}^{\Lambda}$ denotes the degree of circular polarisation of the pure Λ enantiomer of the lanthanide chelate. Values for this quantity have been determined previously: $g_{\mathrm{lum}}^{\Lambda} = +0.45$ for $[\mathrm{Eu(dpa)_3}]^{3-}$ luminescence, wavelength selection 595 nm (bandwidth 4 nm) [25, 26] and $g_{\mathrm{lum}}^{\Lambda} = +0.30$ for $[\mathrm{Tb(dpa)_3}]^{3-}$ luminescence at 543 nm (bandwidth 2 nm). The decay constants k^{Δ} and k^{Λ} can be found from time resolved emission measurement. Note that it is sufficient to determine the average decay constant $k^{\mathrm{av}}(=1/2(k^{\Delta}+k^{\Lambda}))$ which, in cases of small enantioselectivity, can be done by fitting a monoexponential decay function to the experimental data. From k^{av} the average quenching rate constant $k_{\mathrm{q}}{}^{\mathrm{av}}$ can be calculated ($k^{\mathrm{av}} = k_0 + k_{\mathrm{q}}{}^{\mathrm{av}}[\mathrm{Q}]$). Given the values for k_0, k^{av} and $g_{\mathrm{lum}}^{\Lambda}$ are known, E_{q} can be calculated from $g_{\mathrm{lum}}^{\mathrm{cw}}(\lambda)$.

Generally, enantioselectivity in the quenching can arise from a difference in the stability of the two possible diastereomeric encounter complexes formed between the luminophore and quencher, in combination with a difference in the rates for energy transfer within these two encounter complexes. In the case of quenching by vitamin $\mathrm{B_{12}}$ it could be shown that both these factors contribute to the enantioselectivity but that the chiral discrimination in the encounter complex formation is the major factor.[26]

Acknowledgement

This work was supported by the French Ministry of National Education (G.R.).

[1] R. S. Cahn, C. Ingold, V. Prelog, *Angew. Chem.* **1966**, *78*, 413–447; *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 385–415; K. Mislow, *Bull. Soc. Chim. Belg.* **1977**, *86*, 595–601.

[2] K. Mislow, J. Siegel, *J. Am. Chem. Soc.* **1984**, *106*, 3319–3328; E. L. Eliel, *Top. Curr. Chem.* **1982**, *105*, 1–76; J.-C. Chambron, C. O. Dietrich-Buchecker, J.-P. Sauvage, *Top. Curr. Chem.* **1993**, *165*, 131–162.

[3] C. Liang, K. Mislow, *J. Math. Chem.* **1994**, *15*, 35–62; C. Liang, K. Mislow, *J. Math. Chem.* **1994**, *15*, 245–260.

[4] H. L. Frisch, E. Wasserman, *J. Am. Chem. Soc.* **1961**, *83*, 3789–3795; N. Van Gülick, *New J. Chem.* **1993**, *17*, 619–625.

[5] V. I. Sokolov, *Russian Chem. Rev.* **1973**, *42*, 452–463; J. Boeckmann, G. Schill, *Tetrahedron* **1974**, *30*, 1945–1957; G. Schill, G. Doerjer, E. Logemann, H. Fritz, *Chem. Ber.* **1979**, *112*, 3603–3615; D. M. Walba, J. D. Armstrong, A. E. Perry, R. M. Richards, T. C. Homan, R. C. Haltiwanger, *Tetrahedron* **1986**, *42*, 1883–1894.

[6] R. L. Kornegay, H. L. Frisch, E. Wasserman, *J. Org. Chem.* **1969**, *34*, 2030–2031.

[7] J.-C. Chambron, C. O. Dietrich-Buchecker, J.-P. Sauvage, *Comprehensive Supramolecular Chemistry*, *Vol. 9*, "Templating, self-assembly and self-organization" (Eds.: J. P. Sauvage, W. Hosseini), Pergamon, **1996**, 43–83.

[8] C. O. Dietrich-Buchecker, J.-P. Sauvage, *Angew. Chem.* **1989**, *101*, 192–194; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 189–192; C. O. Dietrich-Buchecker, J. Guilhem, C. Pascard, J.-P. Sauvage, *Angew. Chem.* **1990**, *102*, 1202–1204; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1154–1156.

[9] N. C. Seeman, *Acc. Chem. Res.* **1997**, *30*, 357–363.

[10] P. R. Ashton, O. A. Matthews, S. Menzer, F. M. Raymo, N. Spencer, J. F. Stoddart, D. J. Williams, *Liebigs Ann. Chem.* **1997**, 2485–2494.

[11] C. O. Dietrich-Buchecker, J.-P. Sauvage, A. De Cian, J. Fischer, *Chem. Commun.* **1994**, 2231–2232; C. O. Dietrich-Buchecker, G. Rapenne, J.-P. Sauvage, *Chem. Commun.* **1997**, 2053–2054; G. Rapenne, C. O. Dietrich-Buchecker, J.-P. Sauvage, *J. Am. Chem. Soc.* **1999**, *121*, 994–1001.

[12] G. Rapenne, C. O. Dietrich-Buchecker, J.-P. Sauvage, *J. Am. Chem. Soc.* **1996**, *118*, 10932–10933; C. O. Dietrich-Buchecker, G. Rapenne, J.-P. Sauvage, A. De Cian, J. Fischer, *Chem. Eur. J.* **1999**, *5*, 1432–1439.

[13] D. M. Walba, *Tetrahedron* **1985**, *41* , 3161–3212.

[14] M. Meyer, A. M. Albrecht-Gary, C. O. Dietrich-Buchecker, J.-P. Sauvage, *J. Am. Chem. Soc.* **1997**, *119*, 4599–4607.

[15] F. S. Richardson, D. H. Metcalf in *Circular Dichroism, Principles and Applications* (Eds.: K. Nakanishi, N. Berova, R. W. Woody), VCH Publishers, New York, **1994**, pp. 153–177; T. G. Stockman, C. A. Klevickis, C. M. Grisham, F. S. Richardson, *J. Mol. Recognit.* **1996**, *9*, 595–602; see S. C. J. Meskers, H. P. J. M. Dekkers, *J. Am. Chem. Soc.* **1998**, *120*, 6413–6414.

[16] M. R. Everly, D. R. McMillin, *J. Phys. Chem.* **1991**, *95*, 9071–9075.

[17] E. C. Riesgo, A. Credi, L. De Cola, R. P. Thummel, *Inorg. Chem.* **1998**, *37*, 2145–2149.

[18] C. O. Dietrich-Buchecker, J.-P. Sauvage, N. Armaroli, P. Ceroni, V. Balzani, *Angew. Chem.* **1996**, *108*, 1190–1193; *Angew. Chem. Int. Ed. Engl.* **1996**, *108*, 1119–1121.

[19] R. B. Rexwinkel, P. Schakel, S. C. J. Meskers, H. P. J. M. Dekkers, *Appl. Spectrosc.* **1993**, *47*, 731–740.

[20] C. A. Emeis, L. J. Oosterhof, *J. Chem. Phys.* **1971**, *54*, 4809–4819.

[21] K. E. Gunde, A. Credi, E. Jandrasics, A. von Zelewsky, F. S. Richardson, *Inorg. Chem.* **1997**, *36*, 426–434.

[22] S. J. Strickler, R. A. Berg, *J. Chem. Phys.* **1962**, *37*, 814–822.

[23] D. P. Glover-Fischer, D. H. Metcalf, J. P. Bolender, F. S.Richardson, *Chem. Phys.* **1995**, *198*, 207–234 and references therein.

[24] C. L. Maupin, S. C. J. Meskers, H. P. J. M. Dekkers, J. P. Riehl, *J. Phys. Chem. A* **1998**, *102*, 4450–4455 and references therein.

[25] S. C. J. Meskers, M. Ubbink, G. W. Canters, H. P. J. M. Dekkers, *J. Phys. Chem.* **1996**, *100*, 17957–17969.

[26] S. C. J. Meskers, H. P. J. M. Dekkers, *Spectrochim. Acta* **1999**, *55A*, 1857–1874.

Received: November 30, 1999 [F2164]