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CD Spectra of d–f Heterobimetallic Helicates with Segmental Di-Imine Ligands

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We have investigated the CD spectra of a series of enantiomerically pure heterobimetallic helicates, Λ,Λ-[LnCr(**1**)$_3$]$^{6+}$ (Ln = Eu, Gd, Tb), which contain segmental di-imine ligands. For the mononuclear precursor of these helicates, Λ-[Cr(**1**)$_3$]$^{3+}$, a positive exciton couplet was observed around 330 nm, as expected for a tris(di-imine) complex with this absolute configuration. The titration of Ln(III) ions into a solution of this complex leads to the formation of Λ,Λ-[LnCr(**1**)$_3$]$^{6+}$. During this process, the CD signal was observed to invert to give a signal which was negative at lower energies. We investigated the observed changes in the CD spectra using a ZINDO-based computational method which we have previously developed. We were able to show that the exciton coupling of the chromophores coordinated to the Cr and Ln ions give rise to CD signals of *opposite* phase, despite having the same nominal absolute configuration. Exciton coupling between chromophores located on different metal centers ("internuclear" exciton coupling) is also predicted to have a significant impact on the observed spectrum. We were able to "deconstruct" the observed CD spectra into a set of competing exciton coupling effects and show that the sign of these spectra does not correlate with the absolute configuration of the individual metal centers.

Introduction

The assignment of the absolute configuration of the metal centers in complexes of di-imine ligands often relies on the analysis of exciton coupling effects in their CD spectra.[1−3] This is a nonempirical method,[4] and a well-established rule relates the sign of the observed exciton CD curve with the helical chirality of the complex.[2]

For mononuclear complexes, exciton coupling analysis is usually straightforward and the absolute configuration of the metal center can be assigned with confidence. In the past, the exciton coupling analysis of polynuclear complexes has focused exclusively on coupling between chromophores located on the *same* metal center. Recently, however, we have shown that the coupling between chromophores located on *different* metal centers can dominate the observed CD spectra of polynuclear complexes.[5] A ZINDO-based computational method was developed to provide quantitative support to this exciton coupling model. It was shown that the observed CD spectra of polynuclear complexes are often comprised of many competing exciton effects. Therefore, there is the potential for the absolute configurations of the metal centers to be incorrectly assigned if a detailed analysis is not undertaken.

We have used this model to analyze the CD spectra of commonly encountered polynuclear complexes such as helicates and complexes of 2,2′-bipyrimidine (bpm), for example the complex Λ,Λ-[(bipy)$_2$Ru(bpm)Ru(bipy)$_2$]$^{4+}$ which is shown in Figure 1.[5] The intensity of the CD spectra of this complex is anomalously low which could be rationalized by taking into account the exciton coupling of di-imine chromophores located on different metal centers (termed

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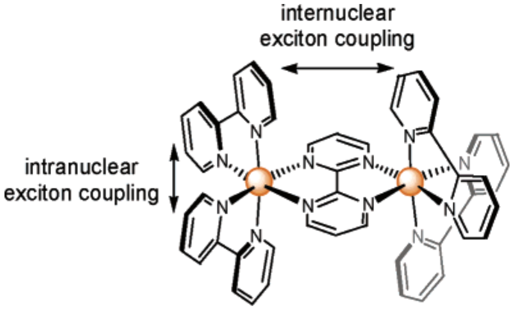
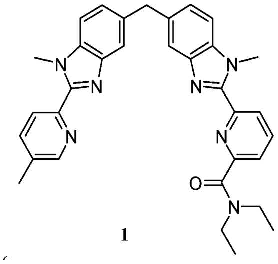


Figure 1. Competing exciton coupling effects in a dinuclear complex of the 2,2′-bipyrimidine bridging ligand.

“internuclear” exciton coupling) as well as that between chromophores located on the same metal center (“intranuclear” exciton coupling).



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Piguet et al. have recently reported[6] the synthesis and characterization of the enantiomerically pure d−f helicates $[\mathrm{LnCr}(\mathbf{1})_3]^{6+}$ (Ln = Eu(III), Gd(III), Tb(III)). As illustrated in Figure 2, the key step in the synthesis of these helicates is the resolution of Λ- and Δ-$[\mathrm{Cr}(\mathbf{1})_3]^{3+}$. The helicity of these inert precursors is strictly maintained upon recombination with Ln(III) to give Λ,Λ-$[\mathrm{LnCr}(\mathbf{1})_3]^{6+}$ and Δ,Δ-$[\mathrm{LnCr}(\mathbf{1})_3]^{6+}$ respectively.

The changes in the CD spectrum associated with the formation of the helicates from their mononuclear precursors were rather surprising (Figure 3).[6] It was observed that the diagnostic positive Cotton effect associated with the low-energy $\pi\rightarrow\pi^*$ transition at 350 nm for Λ-$[\mathrm{Cr}(\mathbf{1})_3]^{3+}$ inverts upon titration with Ln(III) ions *despite the fact that the left-handed helicity of the overall structure is preserved in* Λ,Λ-$[\mathrm{LnCr}(\mathbf{1})_3]^{6+}$.

These anomalous experimental results merit a detailed analysis. Our previous work has shown that the CD spectra of transition metal helicates with related di-imine ligands contain contributions from a variety of exciton coupling modes, both intranuclear and internuclear.[5] Given the close proximity of the chromophores located on different metal centers in the Λ,Λ-$[\mathrm{LnCr}(\mathbf{1})_3]^{6+}$ helicates, we anticipated that their CD spectra would also contain multiple competing effects. The aim of the present report is to rationalize the observed CD spectra of Λ-$[\mathrm{Cr}(\mathbf{1})_3]^{3+}$ and Λ,Λ-$[\mathrm{LnCr}(\mathbf{1})_3]^{6+}$ by assessing the relative contributions made to these spectra by the various exciton coupling modes.

Computational Approach and Methods

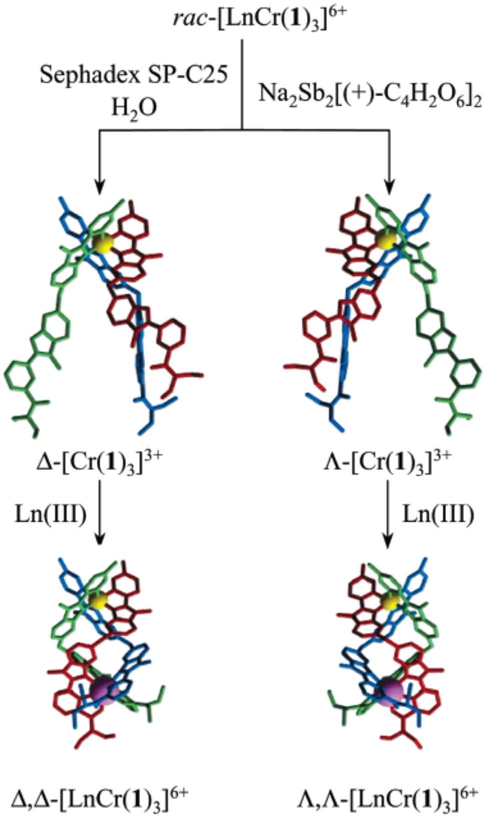

Figure 2. Resolution of $[\mathrm{Cr}(\mathbf{1})_3]^{3+}$ and the synthesis of Δ,Δ-$[\mathrm{LnCr}(\mathbf{1})_3]^{6+}$ and Λ,Λ-$[\mathrm{LnCr}(\mathbf{1})_3]^{6+}$.

Our general computational method has been described in detail elsewhere[5] and follows well-established procedures for the calculation of CD spectra.[7] Essentially, our approach was to calculate[8] the CD curves of chromophore pairs or sets by computing excitation energies and rotational strengths (RS) using the semiempirical ZINDO method.[9] This choice was made on the basis of the large size of the chromophores under investigation, and the fact that this method is known to reproduce the excitation energies of organic chromophores with good accuracy and is particularly well-suited to the calculation of the $\pi-\pi^*$ transitions of N-heterocyclic compounds.[10] Based on our previous calculations on a wide range of complexes,[5] we are confident that our computational method

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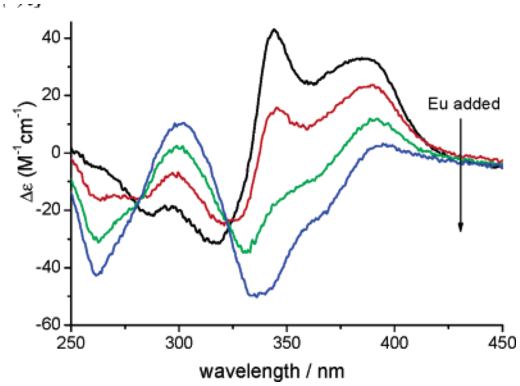

Figure 3. CD titration of Λ-[Cr(**1**)$_3$]$^{3+}$ (black line) with Eu(OTf)$_3$ in CH$_3$CN to give Λ,Λ-[EuCr(**1**)$_3$]$^{6+}$ (blue line). The spectra have been corrected for the incomplete formation of [EuCr(**1**)$_3$]$^{6+}$ by using the known thermodynamic stability constant for this reaction.

leads to reliable estimations of the relative contributions of competing exciton coupling effects in structurally well-characterized and rigid polynuclear complexes of di-imine ligands. We have found that this method leads to accurate predictions of the energy ordering of the positive and negative Cotton effects observed in the region of the $\pi-\pi$ transitions of the di-imine chromophores of these complexes. Given that the overall spectra result from substantial cancellations of positive and negative contributions from individual electronic excitations, however, we do not expect our computational method to be able to quantitatively reproduce the experimental CD spectra across the entire spectrum. Deviations may be particularly acute at higher energies due to the large number of closely spaced excited states. Accordingly, we have focused on the lowest energy $\pi-\pi^*$ transitions of the chromophores (which in general are energetically well-spaced from other transitions), and rather than attempting to reproduce the experimentally observed spectra, our focus has been on probing the relative intensities of the various exciton couplets and developing a general model for the interaction of multiple di-imine chromophores polynuclear complexes. The computational procedure is straightforward, computationally efficient, and easily implemented, and is well suited to high-throughput calculations (useful, e.g., for the calculation of multiple spectra corresponding to different geometries).

Related semiempirical methods have met with good success in dealing with coordination compounds (including the metal ions) and solvent effects,[11] and we are currently exploring ways in which these factors may be accounted for by our model. It is also possible that some of the limitations discussed above may be removed by using a computationally more sophisticated approach such as DFT which has met with success in the reproduction of the CD spectra of transition metal complexes.[12]

The strength of exciton coupling between two chromophores is highly dependent on their relative orientation, thus, for any computational method, the accuracy of the calculated spectra can only be as good as fidelity of the input geometry to the true solution geometry of the complex. This does not present any problems for rigid complexes which have been characterized by X-ray crystallography, however, as is evident from the results in the present report, difficulties may arise if the solution structure is not known with great accuracy. This is another potential source of error in our (and in any other) computational model.

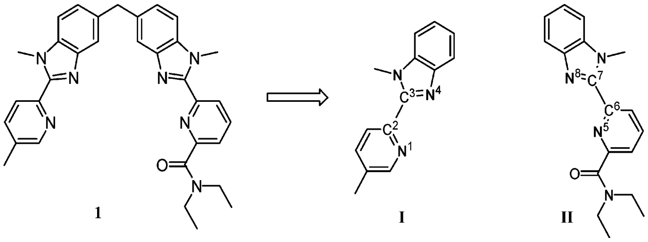

Figure 4. Splitting of ligand **1** into two constituent chromophores **I** and **II**.

Table 1. Excitation Energies Calculated for Chromophores I and II

	Chromophore I			Chromophore II		
	λ/nm	ν/cm^{-1}	f^a	λ/nm	ν/cm^{-1}	f^a
1	333	30052	0.575	357	27993	0.009
2	312	32007	0.006	341	29321	0.657
3	298	33598	0.056	316	31620	0.005
4	280	35780	0.060	305	32812	0.061
5	265	37748	0.086	285	35047	0.110
6	263	37982	0.028	276	36237	0.0323
7	250	39955	0.352	265	37753	0.079

^{a} f = Oscillator strength.

The spectral profile of a single electronic transition is represented by a Gaussian function centered at the excitation energy with an area proportional to the calculated RS. We have used a bandwidth parameter (σ) value of 0.18 eV. Naturally, many electronic transitions are predicted to occur and the overall CD curve is represented by a superimposition of the contributions from the individual transitions. Unless stated otherwise, however, to simplify the calculated CD spectra presented in this paper, we have shown only the CD signals corresponding to the lowest energy $\pi-\pi^*$ transitions of the chromophores. For reference, all calculated rotational strengths are included in the Supporting Information.

Results

Splitting of Ligand 1 Into Two Chromophores and Calculation of their Excitation Energies. For the purpose of analyzing the CD spectra of complexes of ligand **1**, it is convenient to split it into two constituent chromophores, **I** and **II** (Figure 4). The bridging methylene unit of ligand **1** was removed to facilitate the construction of the chromophore models. There are three unique geometries for both chromophores in the X-ray crystal structure of Λ,Λ-[CrEu(**1**)$_3$](OTf)$_6$. For both chromophores, an average chromophore geometry was calculated using these three structures, and this average geometry was used for all the calculations presented in this paper.

The excitation energies of chromophores **I** and **II** were calculated using the ZINDO method, and the results are presented in Table 1. An intense transition is calculated to occur for chromophores **I** and **II** at 333 and 341 nm respectively. These excitations have $\pi-\pi^*$ character, and their transition dipole moments lie in the chromophore plane and nearly parallel to the transannular bonds (C^2−C^3 for **I**, and C^6−C^7 for **II**). These transitions are very similar in nature to the lowest energy $\pi-\pi^*$ transitions of 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen). We may therefore expect that the CD spectra of hypothetical complexes such as *fac*-[M(**I**)$_3$]$^{n+}$ and *fac*-[M(**II**)$_3$]$^{n+}$ would feature intense signals due to the exciton coupling of these transitions,

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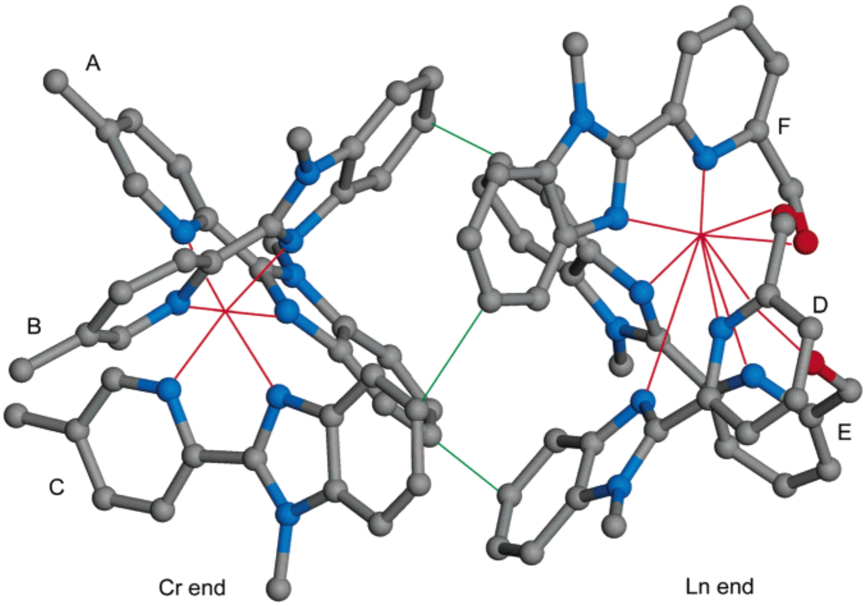

Figure 5. Ligand strands of the X-ray crystal structure of the Λ,Λ-[EuCr($\mathbf{1}$)$_3$](OTf)$_6$ helicate showing the labeling of the individual chromophores. H atoms and the NEt$_2$ groups are removed for clarity. Red lines indicate bonds to the metal centers, and green lines indicate the bridges between the chromophores. Blue, nitrogen; gray, carbon; red, oxygen.

analogous to the signals observed for [M(bipy)$_3$]$^{n+}$ and [M(phen)$_3$]$^{n+}$.[1]

A Model Chromophore System for the Λ,Λ-[LnCr(1)$_3$]$^{6+}$ Helicates. The Λ,Λ-[LnCr($\mathbf{1}$)$_3$]$^{6+}$ helicates may be broken down into a set of individual chromophores. The chromophores at the Cr end of the helicate are labeled A, B, and C, while those at the Ln end of the helicate are labeled D, E, and F (Figure 5). In the following analysis, the A, B, and C chromophores correspond to structure **I**, while the D, E, and F chromophores correspond to structure **II**.

The strength of exciton coupling between two degenerate chromophores is dependent on the relative geometrical orientation of their electric dipole transition moments (edtms) and their separation (see the Supporting Information for the relevant equations). The important geometrical parameters, the angles α, γ, and τ, and the distance R, are described in Figure 6. In the qualitative exciton coupling analysis which follows, we have assumed that α corresponds to C^2−C^3−C$^{3'}$ and C^6−C^7−C$^{7'}$ for **I**/ABC and **II**/DEF respectively, γ corresponds to C$^{2'}$−C$^{3'}$−C^3 and C$^{6'}$−C$^{7'}$−C,^{7} τ corresponds to the C^2-C^3-C$^{3'}$-C$^{2'}$ and C^6-C^7-C$^{7'}$-C$^{6'}$ torsion angles, and R corresponds to the distance between the midpoints of the transannular bonds. These assumptions greatly simplify the analysis as the geometrical parameters can be read directly from coordinates of relevant X-ray crystal structures or model chromophore systems. It should be kept in mind that this choice of the origin of the edtms is somewhat arbitrary, however, and ZINDO calculations show that there is actually a slight deviation (ca. 5°) between the transannular (C^2−C^3 and C^6−C^7) bonds and the direction of the transition moments.

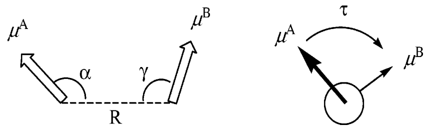

Figure 6. Geometrical parameters describing the relative orientation of the electric dipole transition moments of two chromophores.

Intranuclear Coupling around the Cr Center in Λ-[Cr(1)$_3$]$^{3+}$ and Λ,Λ-[LnCr(1)$_3$]$^{6+}$. The ligand field stabilization energy (LFSE) of chromium(III) complexes is known to be very strong.[13] As a result, the Cr−N bonds in both Λ-[Cr($\mathbf{1}$)$_3$]$^{3+}$ and Λ,Λ-[EuCr($\mathbf{1}$)$_3$](OTf)$_6$ helicate will be strongly directional thus the chromophores will be rigidly held in a certain fixed orientation. We therefore assume that the relative orientation of chromophores A, B, and C in the Λ-[Cr($\mathbf{1}$)$_3$]$^{3+}$ and Λ,Λ-[LnCr($\mathbf{1}$)$_3$]$^{6+}$ complexes *in solution* will be very close to those determined by X-ray crystallography for the Λ,Λ-[EuCr($\mathbf{1}$)$_3$](OTf)$_6$ helicate. The important geometrical parameters which describe the relative orientations of the A, B, and C chromophores in this crystal structure are presented in Table 2.

The sign of the CD signal arising from exciton coupling of these three chromophores can be reliably predicted using qualitative exciton coupling theory.[3] This kind of analysis shows that chromophore set will give rise to a positive exciton couplet.[14] This prediction is in full accord with experimental spectra of Λ-[Cr($\mathbf{1}$)$_3$]$^{3+}$ [6] and with a wide range of other Λ-[M(di-imine)$_3$]$^{2+}$ complexes (where M is an octahedral metal center).[1]

We then proceeded to further investigate the intranuclear exciton coupling around the Cr center of Λ-[Cr($\mathbf{1}$)$_3$]$^{3+}$ and Λ,Λ-[LnCr($\mathbf{1}$)$_3$]$^{6+}$ by using our previously published computational method.[5] A C$_3$-symmetric model of the Cr metal center of these complexes—termed the ABC chromophore model—was constructed by placing three copies of chromophore **I** around a C_3 symmetry axis. The structure of this

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(14) A positive exciton couplet is positive at lower energies and vice-versa for a negative exciton couplet.

Table 2. Selected Geometrical Parameters and Quantitative Exciton Coupling Analysis of the Λ-[Cr(**1**)$_3$]$^{6+}$ Complex, and Selected Geometrical Parameters and Calculated Rotational Strengths for the ABC Chromophore Model System

	X-ray[a] range	X-ray[a] average	ABC model
Geometrical Parameters			
separation (Å)	4.65−4.97	4.85	4.85
α (deg)	66.3−71.2	69.3	68.9
γ (deg)	105.1−109.9	106.9	106.6
τ (deg)	286.5−289.7	72.3	72.4
Qualitative Predictions Based on Exciton Theory			
sign of low E band		positive	
sign of high E band		negative	
Quantitative Predictions Based on ZINDO Calculations			
wavelength (nm)	R. S. (a.u.)		
AB chromophore set			
328.7	1.27		
324.8	−1.01		
ABC chromophore set			
328.1[b]	1.41		
324.2	−1.29		
321.3[b]	0.23		
320.9	−1.34		

[a] X-ray data refers to the crystal structure of Λ,Λ-[EuCr(**1**)$_3$](OTf)$_6$. [b] This rotational strength is doubly degenerate.

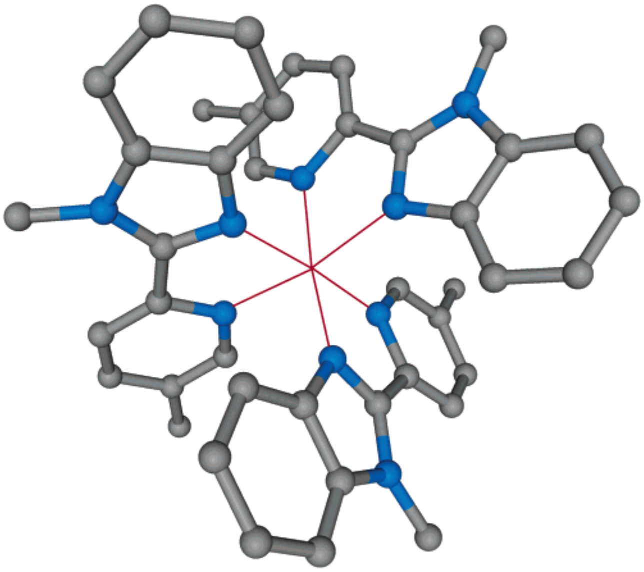

Figure 7. Structure of the ABC chromophore model of the Λ-[Cr(**1**)$_3$]$^{3+}$ complex. The red lines indicate the bonds to the omitted Cr(III) ions. H atoms omitted for clarity. Blue, nitrogen; gray, carbon.

chromophore model is presented in Figure 7. The important geometrical parameters—α, γ, τ, and R—of this model closely match the average values of these parameters seen in the X-ray crystal structure of Λ,Λ-[EuCr(**1**)$_3$](OTf)$_6$ (Table 2).

The CD spectra of both the full ABC chromophore model system and an isolated AB chromophore pair were calculated. Selected calculated rotational strengths are presented in Table 2 and the calculated spectra are shown in Figure 8. In both cases, the results of the calculations agree with qualitative predictions: a pair of oppositely signed rotational strengths appear in the region of the $\pi \rightarrow \pi^*$ transitions centered around 330 nm, with the positive rotational strength being of lower energy.

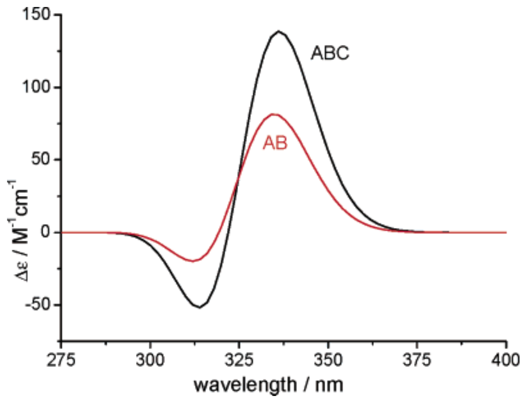

Figure 8. CD spectra calculated for the AB (red) and ABC (black) chromophore model systems.

If we assume that the noncoordinated arms of ligand **1** in the Λ-[Cr(**1**)$_3$]$^{3+}$ complex are free to rotate and therefore make little contribution to the experimental CD spectrum, the ABC chromophore model system serves as a useful model of this complex. Although the calculations are seen to overestimate the intensity of the CD spectrum of Λ-[Cr(**1**)$_3$]$^{3+}$ (see Figure 3), the main spectral features at low energy are well reproduced. The MLCT band centered around 385 nm in the experimental spectrum is, of course, not expected to appear in the theoretical spectrum as the metal ions are excluded from our computational model.

Intranuclear Coupling Around the Ln Center of the Λ,Λ-[LnCr(1)$_3$]$^{6+}$ Helicates. In contrast to the rigid Cr center, the coordination geometry of the Ln(III) center is likely to be rather flexible due to its lack of ligand field stabilization energy. Therefore, although we expect the solution structure of the Λ,Λ-[EuCr(**1**)$_3$]$^{6+}$ helicates to broadly reflect its solid-state structure,[15] there may be significant differences in the exact orientations of the chromophores coordinated to the Ln center. Given this potential discrepancy it was imperative to assess the dependence of the CD curve arising from intranuclear coupling around the Ln center on the relative orientations of the chromophores.

A DE chromophore model was constructed by arranging two copies of chromophore **II** to give a relative orientation which matched the average orientation of these chromophores in the X-ray crystal structure of Λ,Λ-[EuCr(**1**)$_3$](OTf)$_6$ (Table 3). We then investigated the impact of making small changes in either α, γ, or τ on the CD curve calculated for this chromophore pair. It was found that the CD signal was rather invariant to changes in α, however small changes in γ or τ had a significant impact on the calculated curve. Specifically, increases in either γ or τ led to an attenuation of the CD intensity and eventual inversion of the signal to give a negative exciton couplet. This is highlighted by Figure 9 which shows the CD curve calculated for the DE chro-

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Table 3. Selected Geometrical Parameters of the Λ,Λ-[EuCr(**1**)$_3$](OTf)$_6$ Helicate, and Selected Rotational Strengths Calculated for the DE and DEF Chromophore Model Systems

Geometrical Parameters of the Ln End of the Helicate			
	X-ray[a]		
	range	average	ABCDEF model
separation (Å)	5.38−5.90	5.65	5.60
α (deg)	70.2−77.1	74.0	72.2
γ (deg)	115.1−116.9	115.9	116.9
τ (deg)	78.5−90.7	83.4	90.8

Quantitative predictions based on ZINDO calculations	
wavelength (nm)	R. S. (au)
DE chromophore pair	
339.3	−0.49
337.8	0.46
DEF chromophore set	
336.8	−3.26
336.0[b]	1.69[b]

[a] X-ray data taken from the structure of Λ,Λ-[EuCr(**1**)$_3$](OTf)$_6$. [b] This rotational strength is doubly degenerate.

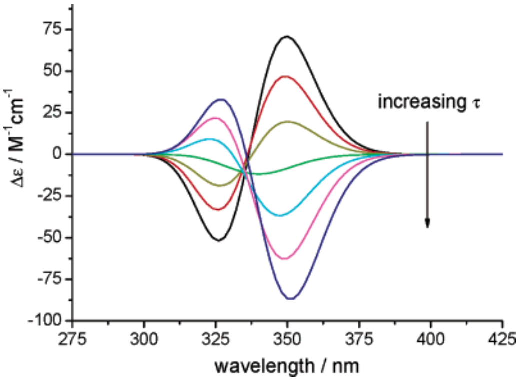

Figure 9. CD curve calculated for the DE chromophore pair for a range of τ values (α and γ were kept constant at 74.1 and 115.9°, respectively). Spectra calculated for $\tau = 75.0°, 80.0°, 85.0°, 90.0°, 95.0°, 100°$, and 105°.

mophore pair for various values of τ in the range 75−105°. α and γ were kept constant at 74.1° and 115.9° respectively. The inversion of the CD signal as τ is increased can be attributed to a switching of the energy ordering of the two intense rotational strengths which appear around 338 nm.[16] It should be emphasized that these CD curves change in sign *without* a formal change to the sense of helicity (i.e., the absolute configuration) of the chromophore set. This effect has been noted previously in the literature.[2]

These calculations imply that the CD spectral intensity arising from intranuclear exciton coupling of D, E, and F chromophores at the Ln end of the Λ,Λ-[LnCr(**1**)$_3$]$^{6+}$ helicates will be extremely sensitive to their relative orientation. As an accurate prediction of the solution-state geometry of these helicates is extremely difficult, we have approached this problem from another direction by posing the following question: which geometries of the Λ,Λ-[LnCr(**1**)$_3$]$^{6+}$ helicates will lead to a calculated CD spectrum which reproduces the experimental spectra?

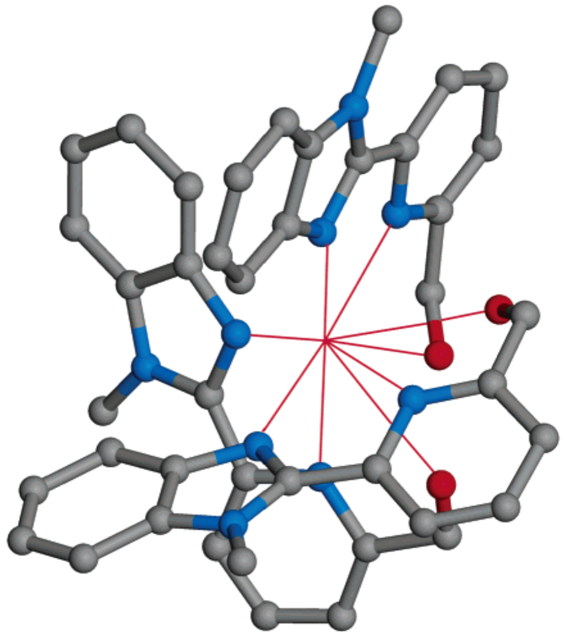

Figure 10. D, E, and F chromophores of the ABCDEF model chromophore system. The red lines indicate the bonds to the omitted Ln(III) ions. H atoms omitted for clarity. Blue, nitrogen; gray, carbon; red, oxygen.

The observed CD spectra of these helicates display a negative band around 340 nm, while the Λ-[Cr(**1**)$_3$]$^{3+}$ complex has a positive peak centered at 350 nm. In terms of individual contributions to the observed spectra of the helicates, this difference can probably be attributed to intranuclear coupling around the Ln center and/or internuclear coupling within the helicate. The results presented above suggest that the DEF chromophore set should have relatively high γ and τ angles as this will lead to CD signals which are negative at lower energies.

A full chromophore model system (ABCDEF) was constructed along these lines with the geometrical parameters listed in Table 3. The values of the γ and τ angles of the D, E, and F chromophores are at the higher end of the range observed in the solid-state structure of Λ,Λ-[EuCr(**1**)$_3$](OTf)$_6$. A diagram showing the arrangement of the D, E, and F chromophores of this model is presented in Figure 10. The geometry of the ABC chromophores (i.e., the Cr end of the helicate) in this model is identical to that in the ABC model discussed above (Table 3). As discussed in more detail below, the relative orientation of the ABC and DEF chromophore sets is similar to that observed in Λ,Λ-[EuCr(**1**)$_3$](OTf)$_6$.

The CD curves calculated for the DE and DEF chromophore sets of the ABCDEF chromophore model are presented in Figure 11, and the calculated rotational strengths in the region of the lowest energy $\pi-\pi^*$ transitions are listed in Table 3. These rotational strengths show that the CD signal will be classical negative exciton couplet centered around ca. 337 nm. The intensity of both curves is rather weak. This is primarily due to the very small energy gap between the oppositely signed rotational strengths which leads to a cancellation of most of the CD signal.

Internuclear Exciton Coupling in the Λ,Λ-[LnCr(1)$_3$]$^{6+}$ Helicates. There are three distinct internuclear exciton

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(16) We do not ascribe any significance to the fact that the spectrum appears to invert at a τ value of around 90 deg. The dependence of the phase of the CD signal on τ is discussed further in the Supporting Information.

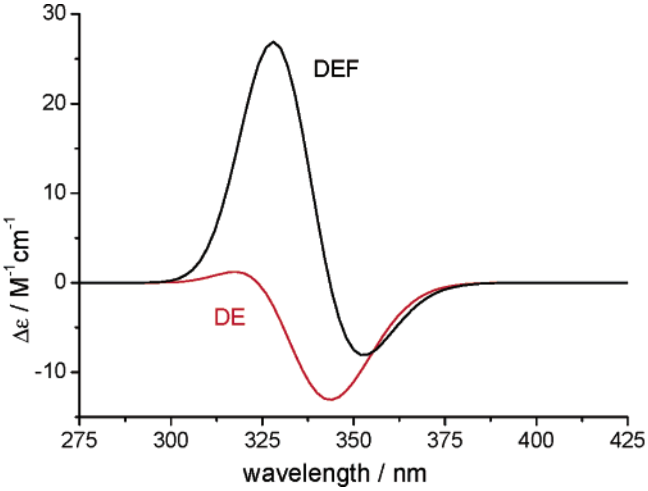

Figure 11. CD curves calculated for the DE (red) and DEF (black) chromophore sets of the ABCDEF chromophore model system.

coupling modes possible within the Λ,Λ-[LnCr(**1**)$_3$]$^{6+}$ helicates: AD, AE, and AF. We have calculated the CD signals arising from these exciton coupling modes by using the ABCDEF model chromophore system described above. The relative orientation of the internuclear chromophore pairs in this model system is very similar to the average of the values seen in the solid-state structure of Λ,Λ-[EuCr(**1**)$_3$](OTf)$_6$ (Table 4). Strictly speaking, these internuclear chromophore pairs should be treated as *nondegenerate* coupled oscillators.[3] The strength of exciton coupling between nondegenerate chromophores is inherently weaker than that between degenerate chromophores,[3] however the calculated excitation energies of the **I** and **II** chromophores (Table 1) imply that their lowest energy $\pi-\pi^*$ transitions are close enough in energy to allow significant coupling.

The CD curves calculated for the isolated AD, AE, and AF internuclear chromophore pairs of the ABCDEF chromophore model system are presented in Figure 12. The AD chromophore pair exhibits a very intense curve in the region of the lowest energy $\pi-\pi^*$ transition. The AE and AF chromophore pairs lead to CD signals of lower intensity which have phase opposite of the AD pair. Therefore, the overall contribution of the internuclear coupling modes is likely to be a moderately intense signal which is negative at lower energies. Importantly, the CD signal arising from the AD pair was found to be relatively invariant to small (±10°) changes in α, γ, and τ.

Contribution of the Various Intra- and Internuclear Exciton Coupling Effects to the Observed CD Spectra of the [LnCr(1)$_3$]$^{6+}$ Helicates. The results discussed above can be combined to "reconstruct" the observed CD spectra of Λ-[Cr(**1**)$_3$]$^{3+}$ and Λ,Λ-[LnCr(**1**)$_3$]$^{6+}$. In a greatly simplified fashion, the various exciton coupling effects which are expected to dominate these spectra are presented schematically in Figure 13.[17]

Table 4. Selected Geometrical Parameters of the Λ,Λ-[EuCr(**1**)$_3$](OTf)$_6$ Helicate, and Selected Rotational Strengths Calculated for the AD, AE, and AF Chromophore Model Systems

Geometrical Parameters of Internuclear Exciton Pairs

	X-ray[a]		
	range	average	model[b]
	AD pair		
separation (Å)	10.19−10.48	10.33	10.30
α (deg)	130.4−136.7	132.8	131.8
γ (deg)	132.4−135.6	134.5	132.6
τ (deg)	306.2−319.4	311.9	314.3
	AE pair		
separation (Å)	8.95−9.28	9.09	9.03
α (deg)	106.6−114.7	111.7	110.0
γ (deg)	112.2−118.3	116.0	114.3
τ (deg)	235.2−256.7	245.7	246.1
	AF pair		
separation (Å)	8.20−9.23	8.78	8.77
α (deg)	145.4−155.6	151.8	152.2
γ (deg)	143.3−146.7	145.2	142.0
τ (deg)	125.7−164.6	144.3	141.9

Quantitative predictions based on ZINDO calculations

wavelength (nm)	R. S. (au)
AD chromophore pair	
357.2	−0.08
347.7	−1.12
331.6	0.54
AE chromophore pair	
357.3	−0.05
342.6	0.09
327.3	0.03
AF chromophore pair	
357.6	−0.05
343.8	0.03
328.9	−0.24

[a] X-ray data taken from the structure of Λ,Λ-[EuCr(**1**)$_3$](OTf)$_6$. [b] These values refer to the ABCDEF chromophore model.

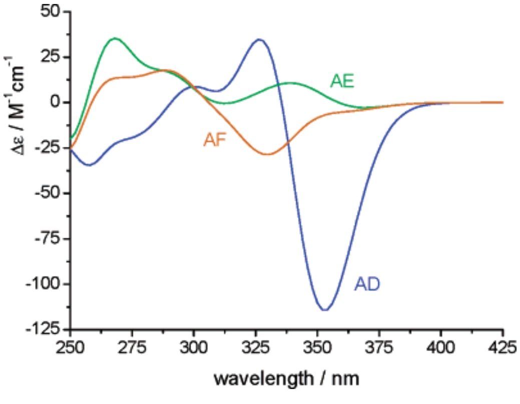

Figure 12. CD curves calculated for the AD (blue), AE (green), and AF (orange) chromophore pairs of the ABCDEF chromophore model system. Because distinct exciton couplets were not immediately apparent from the calculated rotational strengths of the AE and AF chromophore pairs, *all* calculated rotational strengths were used to draw the presented curves.

(i) The relative orientation of the chromophores in the ABC model system closely matches the average geometry of the corresponding chromophore in the X-ray crystal structure of Λ,Λ-[EuCr(**1**)$_3$](OTf)$_6$. Qualitative and quantitative exciton coupling analyses both show that this chromophore set will give rise to a positive exciton couplet

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(17) The experimental spectrum will contain contributions from many other sources of CD intensity, for example due to the internal chirality of the chromophores, the coupling of higher-order multipoles, and metal-centered transitions, etc. We expect, however, that the exciton coupling effects discussed here will be the dominant contributions.

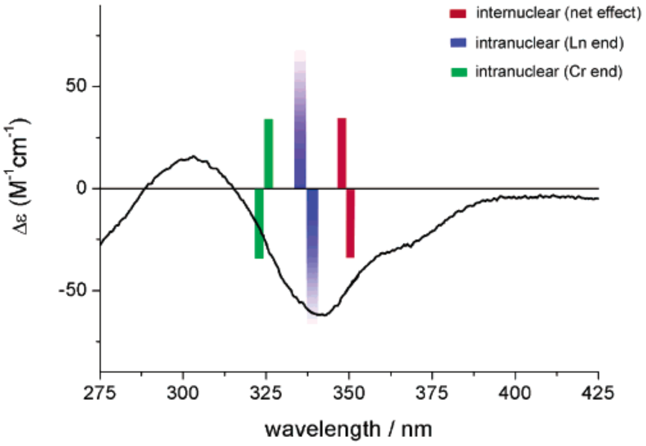

Figure 13. Schematic summarizing the dominant exciton coupling effects in the CD spectra of Λ,Λ-[LnCr(**1**)$_3$]$^{6+}$. The black line corresponds to the CD spectrum of Λ,Λ-[GdCr(**1**)$_3$]$^{6+}$ measured in CH$_3$CN.

(shown in green in Figure 13). This is in full accord with the observed CD spectrum of Λ-[Cr(**1**)$_3$]$^{3+}$ (Figure 3).

(ii) A series of calculations showed that the CD signal arising from the exciton coupling of the chromophores coordinated to the Ln ion of the [LnCr(**1**)$_3$]$^{6+}$ helicates is extremely sensitive to the relative orientation of the chromophores, in particular the angles γ and τ. Higher values of these angles lead to CD curves which are more negative at lower energies. The calculated CD curve of a DEF chromophore model in which these angles are at the upper ends of the range observed in the solid-state structure of Λ,Λ-[EuCr(**1**)$_3$](OTF)$_6$ displays a negative exciton couplet. This is depicted in blue in Figure 13, and the faded lines emphasize that the fact that contribution of this signal to the overall spectrum cannot be accurately predicted without more detailed knowledge of the solution state geometry. We have taken steps toward addressing this point by performing a geometry optimization on a simplified model of the [EuCr(**1**)$_3$]$^{6+}$ helicate, as detailed in the Supporting Information. The results of these calculations imply that high values of γ and τ will indeed be favored. Furthermore, the energetic barrier to changes in τ is predicted to be low, therefore a range of conformations will be thermally accessible.

(iii) The CD signals arising from the three internuclear exciton coupling modes in a full ABCDEF model system were calculated. The net effect of these internuclear coupling modes is predicted to be a CD curve which is strongly negative at lower energies.

(iv) Given the uncertainty concerning the exact solution state geometry of the helicates, any direct calculation of their spectra is expected to be rather imprecise. We may, however, reconstruct their CD spectra and rationalize the CD signal inversion seen in Figure 3 in the following way. If we assume that the angles γ and τ of the chromophores coordinated to the Ln center adopt values which are at the upper ends of the range observed in the solid-state structure of Λ,Λ-[EuCr(**1**)$_3$](OTF)$_6$, then both the CD signal arising from intranuclear coupling at the Ln end of the Λ,Λ-[LnCr(**1**)$_3$]$^{6+}$ helicates *and* the net signal from the intranuclear coupling modes are predicted to be of opposite phase to internuclear coupling around the Cr center. These two components are shown in blue and red, respectively, in Figure 13. These components are expected to dominate the observed spectra of Λ,Λ-[LnCr(**1**)$_3$]$^{6+}$ thereby leading to an overall signal which is negative at lower energies. With respect to the CD titration presented in Figure 3, the three internuclear exciton coupling modes *and* the intranuclear coupling around the Ln ion will be switched on when the Ln(III) ions are added to Λ-[Cr(**1**)$_3$]$^{3+}$ to form Λ,Λ-[LnCr(**1**)$_3$]$^{6+}$. Therefore, the intensity of the spectra will be attenuated and the signal will eventually invert during the titration.

(v) The relative intensities of the CD spectra of the Λ,Λ-[LnCr(**1**)$_3$]$^{6+}$ helicates is observed to be inversely proportional to the size of the Ln ion, decreasing in the order Tb > Gd > Eu.[6] This observation lends further support to our contention that exciton coupling of the chromophores coordinated to the Ln ion produces a negative exciton couplet. Smaller lanthanide ions will hold the chromophores at this end of the helicate closer together thereby strengthening this mode of exciton coupling which in turn will lead to an increase in the amplitude of the observed CD spectrum.

(vi) The full ABCDEF chromophore set represents a model of the Λ,Λ-[LnCr(1)$_3$]$^{6+}$ helicates, thus we may make a direct calculation of its CD spectrum using this model. The resulting spectrum displays a negative peak at low energies (Figure S1), in accord with the experimental spectra of the helicates. The experimental spectrum is less well reproduced at higher energies, however better agreement could certainly be achieved by fine-tuning the relative orientation of the D, E, and F chromophores.

Conclusion

The CD spectra of Λ-[Cr(**1**)$_3$]$^{3+}$ and Λ,Λ-[LnCr(**1**)$_3$]$^{6+}$ helicates constituted an ideal model for the further extension of our recently reported theoretical approach to the CD spectra of complexes of di-imine ligands. Using a simple chromophore model system, we were able to deconstruct the observed spectra into a set of competing exciton coupling effects. We were thus able to rationalize the inversion of the CD signal observed during the conversion of Λ-[Cr(**1**)$_3$]$^{3+}$ to Λ,Λ-[LnCr(**1**)$_3$]$^{6+}$, and we may conclude that our computational model is suitable for the analysis of heterobimetallic helicates with substituted di-imine ligands.

One particularly salient point arising from this analysis is that the sign of observed CD spectrum of Λ,Λ-[LnCr(**1**)$_3$]$^{6+}$ *cannot be directly correlated with the absolute configuration of the metal centers*.[18] This is primarily due to the strength of exciton coupling between chromophores which are coordinated to different metal centers, and that the net effect of these coupling modes is of phase opposite to the intranuclear coupling at the Cr end of the helicate. Further, the CD signal arising from intranuclear exciton coupling around the Ln ion appears to be rather weak and in phase with the net signal of internuclear coupling modes.

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(18) These results stand in contrast to those obtained for related D$_3$-symmetric helicates where the intranuclear exciton coupling signal from each end of the helicate is necessarily identical and is far more intense that the internuclear signal (ref 5). In such cases, the absolute configuration of the metal centers is still reflected by the sign of the observed CD spectrum.

The CD spectrum of Λ,Λ-[LnCr(**1**)$_3$]$^{6+}$ is extremely sensitive to small structural changes from the average geometry determined by X-ray crystallography for Λ,Λ-[LnCr(**1**)$_3$](OTf)$_6$. For certain chromophore pairs, the dependence of the calculated CD spectrum on the geometry was so acute that essentially mirror-image CD signals could be obtained by using the upper or lower crystallographically determined values of certain geometrical parameters. This situation presents a particular challenge as, unlike for very rigid complexes, the solution structure of the helicate cannot be assumed to parallel the solid-state structure. We addressed this issue by making an assumption about the solution-state geometry which could be justified on the basis of the dependence of the CD spectral intensity on the size of the Ln ion, and which was supported by DFT calculations on a model Eu(III) complex. In other cases, however, a direct assessment of the solution geometry may be required for a rigorous analysis of the CD spectrum.

Supporting Information Available: The CD curve calculated for the full ABCDEF chromophore set, a discussion of the dependence of the strength of exciton coupling of two chromophores on their relative orientation, the geometry optimization of a model Eu(III) complex and the dependence of its potential energy on τ, and coordinates of the ABCDEF model system and full tables of calculated rotational strengths are included as Supporting Information (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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