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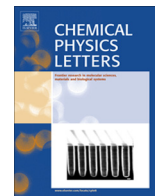


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Explanation of the sign inversion in the magnetic circular dichroism of Möbius [28] hexaphyrin



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ABSTRACT

Meso-phenyl hexaphyrin is an extended annulene system which can adopt both Hückel and Möbius topologies based on the oxidation state. In this contribution we analyze the remarkable sign inversion of the MCD spectrum which accompanies this topological switch. The treatment is based on the identification of the circular wave assignments of the relevant excited states; the corresponding magnetic moments are calculated using the CASCI (4,4) approach. In this approach wavefunctions are obtained from configuration interaction in the active space of the four Kohn–Sham frontier orbitals of the chromophore. The results reproduce the signs of the MCD spectra. The anomalous sign in the Möbius conformation is attributed to the quenching of the excited state orbital moment by the ring twist.

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1. Introduction

Extended porphyrins with more than five pyrrolic units have the unique property that they can occur both in a planar and in a twisted Möbius conformation. Meso-aryl-substituted hexaphyrins with six pyrroles can switch between the two forms depending on the oxidation state [1]. In the oxidized 26 π -electron state they adopt a planar aromatic ring structure, in line with the Hückel $4n + 2$ rule. However in the reduced 28 π -electron state the planar annulene is anti-aromatic and can achieve a stable closed shell configuration by a Hückel-to-Möbius topological switch [2,3]. It was observed that this switch to a twisted form could take place spontaneously in solution. Magnetic Circular Dichroism (MCD) spectra of the Hückel [26]-hexaphyrin and Möbius [28]-hexaphyrin showed a remarkable sign inversion of the MCD signal associated with the dominant Soret absorption band. In Ref. [1] absorption spectra were characterized on the basis of ZINDO/S calculations and DFT orbitals were presented. The MCD spectra were discussed only qualitatively, and it was indicated that no theory for the absolute MCD sign of Möbius aromatic molecules was available. In the present contribution we have analyzed this inversion using a Complete Active Space Configuration Interaction (CASCI) calculation, based on Kohn–Sham frontier orbitals. This approach was shown to be successful in predicting signs of MCD spectra for subporphyrins [4].

2. Methods

Figure 1 shows the two oxidation states of the hexaphyrin, [26] and [28]. In the X-ray structure of [28] tautomerism of the pyrrole-proton is observed, due to hydrogen bonding with co-crystallized ethanol. The actual systems carry *meso*-aryl substituents. Dihedral angles of these substituents are close to 90°, which minimizes the overlap of their π -electron cloud with the central π -system. ZINDO and Time-Dependent Density Functional Theory (TDDFT) calculations confirm that these substituents do not influence the relevant transitions. We omitted these aryl substituents to facilitate the calculation. First the geometry optimization was performed using the hybrid B3LYP functional and a 6-311+G (d,p) basis set in the GAUSSIAN09 package [5]. Subsequent calculations on these geometries included calculations of UV–vis spectra using TDDFT, also with B3LYP/6-311+G (d,p) model, and calculations of Nuclear Independent Chemical Shift (NICS) values on GIAO-B3LYP/6-311+G (d,p) level of theory. For calculations of magnetic dipole momenta the MOLCAS package was used [6]. Single-point CASCI (4,4) calculations on DFT optimized geometries were performed using the B3LYP orbitals and a 6-31G (d,p) basis set, as described previously [4]. The gauge origin is chosen at the center of the annulene, which reduces the error due to gauge-dependence [7].

3. MCD spectroscopy

Circular dichroism (CD) is defined as the difference in intensity between left and right circular polarized light. In natural CD this

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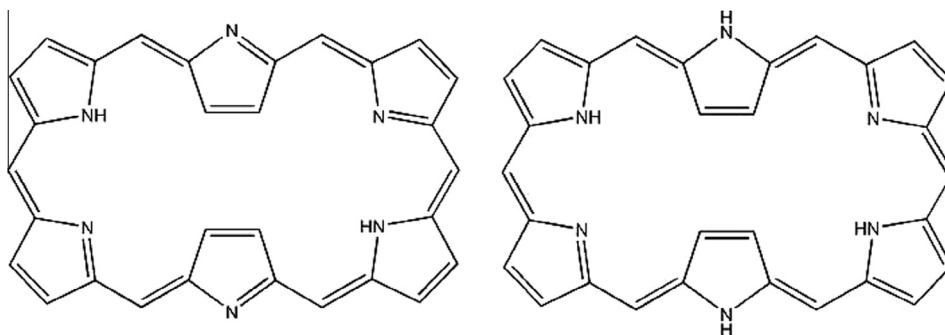


Figure 1. [26]Hexaphyrin (left) and [28]hexaphyrin (right).

difference is related to the helicity of the charge that is transferred in the excitation. A helix is formed when a translation is coupled to a rotation about the axis of translation, hence natural CD requires that the electric and magnetic transition dipoles are aligned, as is expressed by the Rosenfeld equation for the CD intensity [8]. It can only arise in chiral molecules. In magnetic CD the dichroism is measured in the presence of a strong magnetic field parallel to the direction of propagation of the light. The field causes a splitting of degenerate states due to the Zeeman effect. CD can then arise due to the coupling between the resulting magnetic dipole and electric transition dipoles for circular polarized light. For the case of annular molecules with a closed shell ground state and a two-fold degenerate excited state the CD spectrum has the appearance of the derivative of a Gaussian absorption curve with wings of equal intensity. In MCD theory this is described by the \mathcal{A}_1 parameter [9].

$$\mathcal{A}_1 \sim \langle J_0 | m_{-1} | J_{+1} \rangle \langle J_{+1} | \hat{L}_z | J_{+1} \rangle \langle J_{+1} | m_{+1} | J_0 \rangle - \langle J_0 | m_{+1} | J_{-1} \rangle \langle J_{-1} | \hat{L}_z | J_{-1} \rangle \langle J_{-1} | m_{-1} | J_0 \rangle \quad (1)$$

Here J_0 is the nondegenerate ground state and $J_{\pm 1}$ denote the excited state Zeeman components. The central matrix element is the angular momentum part of the Zeeman operator. The \mathcal{A}_1 quantity is thus a measure for the magnetic moment of the excited states. If the excited state is nondegenerate this moment will be zero. However in this case second-order Zeeman interactions give rise to a magnetic response term, which is incorporated in MCD theory by the B_0 parameter. One has for a transition $J_0 \rightarrow J_x$:

$$B_0 \sim \sum_K \frac{\langle J_0 | m_{-1} | J_x \rangle \langle J_x | \hat{L}_z | K \rangle \langle K | m_{+1} | J_0 \rangle}{\Delta E_{KJ_x}} - \sum_K \frac{\langle J_0 | m_{+1} | J_x \rangle \langle J_x | \hat{L}_z | K \rangle \langle K | m_{-1} | J_0 \rangle}{\Delta E_{KJ_x}} \quad (2)$$

The summation runs over all excited states K which are magnetically coupled to J_x . The denominator in this expression is the energy difference between K and J_x . In case J_x forms together with J_y the components of a parent level that would be degenerate in the ideal symmetry case, the principal term in the summation will be restricted to $K = J_y$ and *vice versa* for the transition $J_0 \rightarrow J_y$. The MCD spectrum for this band system will thus consist of two Faraday B-terms with opposite signs. If the splitting between the two components is small, the convoluted MCD spectrum will acquire the derivative shape of an overall A-term, with wings of equal intensity. Such a case is indicated as a pseudo-A term. The magnetic orbital moments survive as the off-diagonal Zeeman interactions between the respective components. This behaviour is seen in the MCD spectra of the hexaphyrins in the present study.

4. Results

[26] Hexaphyrin presents several conformations discussed in details in [1]. The structure shown in Figure 1, although not the most stable one in unsubstituted hexaphyrins, is the one that preserves the ring conformation corresponding to the experimentally observed *meso*-aryl-substituted hexaphyrins. This conformation is

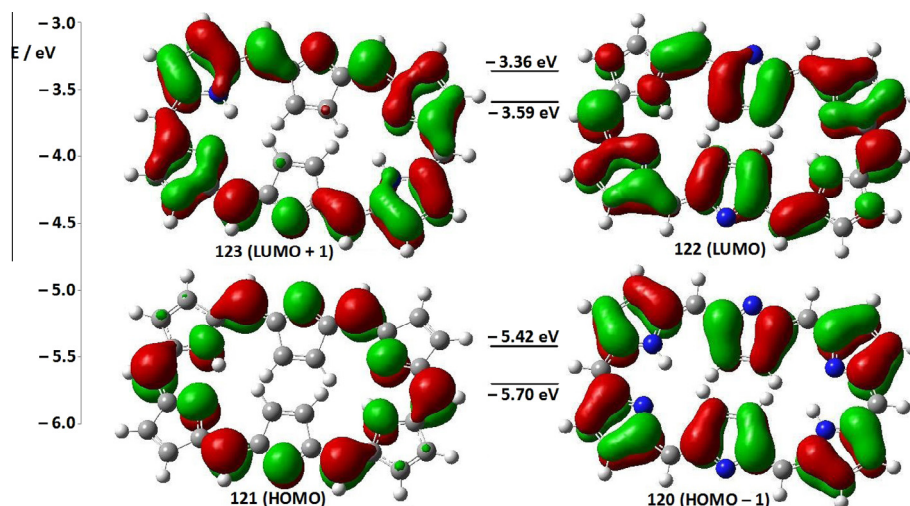


Figure 2. Four frontier molecular orbitals of Hückel [26]hexaphyrin (isocontour value is 0.02).

Table 1

Four lowest singlet excitations of Hückel [26]hexaphyrin obtained by TDDFT. Comparison of TDDFT and CASCI coefficients.

Excited state	λ/nm	Osc. strength	Composition	TDDFT	CASCI
Ψ_1	866	0.0324	121 \rightarrow 122	0.5765	0.5184
			120 \rightarrow 123	0.3830	0.7824
Ψ_2	769	0.0015	120 \rightarrow 122	0.5061	0.6375
			121 \rightarrow 123	−0.4715	−0.6840
Ψ_3	511	0.5115	119 \rightarrow 122	0.5063	
			120 \rightarrow 123	−0.4190	−0.4425
			121 \rightarrow 122	0.2489	0.6958
Ψ_4	496	0.7416	121 \rightarrow 123	0.5109	0.5554
			120 \rightarrow 122	0.4823	0.6026

nearly planar and presents a quite effective π -conjugation and an aromatic character reflected in a NICS value at the center of the ring of -17.3 . A closer look at the orbital picture (see Figure 2) shows clear separation of HOMO and LUMO levels. The splittings are almost identical to the results of Sankar et al. [1], which included the phenyl-substituents. The TDDFT absorption spectrum is described in Table 1. The measured absorption spectrum of the phenyl-substituted chromophore has an intense band at 567 nm, with a shoulder at 590 nm, which correspond to transitions to Ψ_4 and Ψ_3 respectively. The difference with the calculated energies is in the order of approx. 80 nm. TDDFT calculations at a lower 6-31G* level, but with the six aryl-substituents, reduce this error to approx. 50 nm. The spectrum is typical for an aromatic molecule. The composition of excitations, calculated by TDDFT and by CASCI, can be correlated with the composition that arises in the Gouterman's four orbital model [10]. In the equatorial plane the x -direction is laid along the short axis, and the y -direction along the long axis. Starting at the pyrrole nitrogen on the short axis and going around the perimeter of the ring the π -type HOMO orbital changes sign twelve times, corresponding to a $\cos(6\phi)$ circular wave. The cyclic orbital parentage of the HOMO is thus denoted as $c6$. The HOMO-1 varies as the corresponding $\sin(6\phi)$ wave and is denoted as $s6$. Similarly the LUMO and LUMO+1 are characterized by 14 sign changes and thus match a ring quantum number equal to 7. They correspond to $s7$ and $c7$ respectively. The first two excitations belong to the Q -band, where the orbital and hole momenta are added to a formal $\Lambda = 13$ excited state. The next two

correspond to the B -band of the spectrum, where the two momenta are subtracted to a formal $\Lambda = 1$ system. Then the four excited states correspond to the following components:

$$\begin{aligned}\Psi_1 &= [(121 \rightarrow 122) + (120 \rightarrow 123)] = [(c6 \rightarrow s7) + (s6 \rightarrow c7)] = Q_y \\ \Psi_2 &= [(120 \rightarrow 122) - (121 \rightarrow 123)] = [(s6 \rightarrow s7) - (c6 \rightarrow c7)] = -Q_x \\ \Psi_3 &= [(121 \rightarrow 122) - (120 \rightarrow 123)] = [(c6 \rightarrow s7) - (s6 \rightarrow c7)] = B_y \\ \Psi_4 &= [(121 \rightarrow 123) + (120 \rightarrow 122)] = [(c6 \rightarrow c7) + (s6 \rightarrow s7)] = B_x\end{aligned}\quad (3)$$

The MCD spectrum for each band system corresponds to two Faraday B terms. The off-diagonal Zeeman interactions between the respective components take the form of magnetic orbital moments. In the perimeter model these are identified as the angular momenta of the Q - and B -band, and are denoted resp. as L and ℓ parameters [11]. Computation of these matrix elements with the CASCI (4,4) formalism, based on the DFT orbitals yields:

$$\begin{aligned}L &= i\langle Q_x | \hat{L}_z | Q_y \rangle = i\langle -\Psi_2 | \hat{L}_z | \Psi_1 \rangle = 6.7h \\ \ell &= i\langle B_x | \hat{L}_z | B_y \rangle = i\langle \Psi_4 | \hat{L}_z | \Psi_3 \rangle = 0.11h\end{aligned}\quad (4)$$

The two band systems are predicted to have the shape of a pseudo-A term, with a *normal* sign pattern, i.e. a $-$, $+$ sign sequence with increasing energy. As compared to the ideal cyclic values $L = 13h$ and $\ell = 1h$, the actual values show a substantial quenching, which is typical for annulene systems and is due to the projection of the cyclic waves on the atomic basis set [12].

[28] Hexaphyrin is stable in a Möbius conformation. DFT calculations favor the twisted form over the planar Hückel form by 1–3 kcal/mol, depending on the tautomer considered [3]. Furthermore the Möbius structure is aromatic with a NICS value of -14.89 at the center of the ring, whereas the Hückel conformation is anti-aromatic with a NICS value of $+43.38$. The frontier molecular orbitals are shown in Figure 3, and the corresponding singlet excitations are listed in Table 2. Overall the spectrum exhibits the same pattern as the planar [26] form, with a lower Q -band system of very weak intensity (1100–700 nm) and a strong Soret region at 591 nm, with a shoulder at 620 nm.

When determining the formal angular momentum of the frontier orbitals by counting angular nodes, the twisted topology entails that one must go around twice to reach the starting point again [13]. Accordingly, the orbital patterns are characterized by

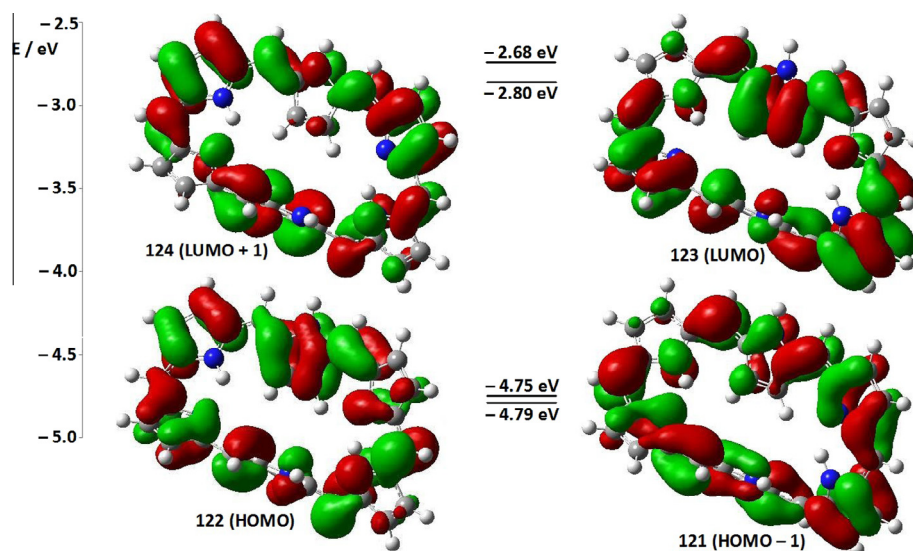


Figure 3. Four frontier molecular orbitals of Möbius [28]hexaphyrin (isocontour value is 0.02).

Table 2

Four lowest singlet excitation of Möbius [28]hexaphyrin obtained by TDDFT. Comparison of TDDFT and CASCI coefficients.

Excited state	λ/nm	Osc. strength	Composition	TDDFT	CASCI
Φ_1	862	0.0011	122 \rightarrow 123	−0.4052	−0.4796
			121 \rightarrow 123	0.3542	0.4284
			121 \rightarrow 124	−0.3271	−0.5106
			122 \rightarrow 124	−0.3201	−0.5400
Φ_2	813	0.0028	121 \rightarrow 123	0.3843	0.4594
			122 \rightarrow 123	0.3625	0.4801
			122 \rightarrow 124	−0.3509	−0.5354
			121 \rightarrow 124	0.3107	0.5003
Φ_3	529	0.5404	121 \rightarrow 124	0.5060	0.5799
			122 \rightarrow 123	−0.4249	−0.5952
Φ_4	490	1.7019	122 \rightarrow 124	−0.4775	−0.5498
			121 \rightarrow 123	−0.4418	−0.6788

half-integral ring quantum numbers. As an example in following the π orbital path of the HOMO-1, one counts 26 nodal points when going around twice. This corresponds to the variation of the argument $\frac{13}{2}\phi$ in the interval $[0, 4\pi]$, as is expected for a 28-electron Möbius system. Now is this a cos or a sin function? This depends on where we put the origin of the ring coordinate ϕ . The only starting point for the angle ϕ that offers a clear canonical distinction between the two components is the pyrrole NH group in the upper left corner of the Möbius band. This direction follows an approximate twofold symmetry axis which runs through the twist region. So we have taken this direction as the x-axis. It corresponds approximately to the long axis direction. The HOMO-1 clearly varies as $\cos(\frac{13}{2}\phi)$, and thus will be denoted as $c_{\frac{13}{2}}$. The HOMO level transforms as the corresponding $s_{\frac{13}{2}}$ function; the LUMO and LUMO+1 change sign 30 times when going around twice, and thus have nodal characteristics of angular momentum $\frac{15}{2}$. They transform as $c_{\frac{15}{2}}$ and $s_{\frac{15}{2}}$ respectively. The coupling of these orbital momenta is thus predicted to yield momenta of 14 and 1 \hbar . The transitions are thus as follows:

$$\begin{aligned}
 \Phi_1 &\approx [-(122 \rightarrow 123) - (121 \rightarrow 124) + (121 \rightarrow 123) - (122 \rightarrow 124)] \\
 &= [-(s_{\frac{13}{2}} \rightarrow c_{\frac{15}{2}}) - (c_{\frac{13}{2}} \rightarrow s_{\frac{15}{2}}) + (c_{\frac{13}{2}} \rightarrow c_{\frac{15}{2}}) - (s_{\frac{13}{2}} \rightarrow s_{\frac{15}{2}})] \\
 &= \frac{1}{\sqrt{2}}(Q_x - Q_y) \\
 \Phi_2 &\approx [(122 \rightarrow 123) + (121 \rightarrow 124) + (121 \rightarrow 123) - (122 \rightarrow 124)] \\
 &= [(s_{\frac{13}{2}} \rightarrow c_{\frac{15}{2}}) + (c_{\frac{13}{2}} \rightarrow s_{\frac{15}{2}}) + (c_{\frac{13}{2}} \rightarrow c_{\frac{15}{2}}) - (s_{\frac{13}{2}} \rightarrow s_{\frac{15}{2}})] \\
 &= \frac{1}{\sqrt{2}}(Q_x + Q_y) \\
 \Phi_3 &= [(121 \rightarrow 124) - (122 \rightarrow 123)] = [(c_{\frac{13}{2}} \rightarrow s_{\frac{15}{2}}) - (s_{\frac{13}{2}} \rightarrow c_{\frac{15}{2}})] = B_y \\
 \Phi_4 &= [-(122 \rightarrow 124) - (121 \rightarrow 123)] = [-(s_{\frac{13}{2}} \rightarrow s_{\frac{15}{2}}) - (c_{\frac{13}{2}} \rightarrow c_{\frac{15}{2}})] = -B_x
 \end{aligned}
 \tag{5}$$

The matrix elements of the magnetic dipole moment between the components are calculated as:

$$\begin{aligned}
 L &= i\langle Q_x | \hat{l}_z | Q_y \rangle = i\langle \Phi_1 | \hat{l}_z | \Phi_2 \rangle = 3.4\hbar \\
 \ell &= i\langle B_x | \hat{l}_z | B_y \rangle = i\langle \Phi_3 | \hat{l}_z | \Phi_4 \rangle = -0.09\hbar
 \end{aligned}
 \tag{6}$$

According to these results one expects a pseudo-A term in the Soret region with an inverted sign as compared to the planar [26] Hückel hexaphyrin. This is indeed observed in the MCD spectra [1].

5. Discussion

Both the [26] and [28] configurations clearly illustrate the success of the respective Hückel and Möbius electron counting rules for aromatic electronic structures. The TDDFT calculations on the unsubstituted hexaphyrins are in line with the previous results [1]. Note a switch of polarization of the Soret components in the [26] and [28] compounds: the long-wavelength shoulder is

polarized along the long-axis direction for [26], but along the short axis for [28]. This switch is not reproduced by the ZINDO calculations, which predict short-axis polarization for the long-wavelength shoulder in both compounds. At the DFT level the relevant Ψ_3 excited state for [26] has a significant contribution from the transition (119 \rightarrow 122) involving the HOMO-2, which is not present in the ZINDO calculation (see Table 1).

The present contribution is aiming at explaining the sign inversion in the principal MCD spectra. The calculations point to a clear difference in the magnetic moment associated with the Soret excited state. For the Hückel [26] hexaphyrin the ℓ value shows a typical pronounced reduction as compared to the particle on a ring value, but nevertheless remains positive. In contrast in the Möbius hexaphyrin the quenched value is negative. In order to further elucidate the switch in the sign of the magnetic moment for the ℓ -parameter we have evaluated the separate magnetic moments of the HOMO and LUMO manifolds. To this aim we calculated the off-diagonal matrix elements of magnetic momenta between the ground state and first excited states in the *dication* and the *dianion*. For the dication the excitation corresponds to the transition from the original HOMO-1 to HOMO; for the dianion it corresponds to the transition between the original LUMO and LUMO+1. For this purpose, the above calculations were conducted on frozen geometries of hexaphyrins 2+ and 2-. For [26] hexaphyrin the matrix elements are 3.6 \hbar in the HOMO level and 4.7 \hbar in the LUMO level. For [28]hexaphyrin the same matrix elements are 5.3 \hbar and 4.6 \hbar respectively. This clearly shows that the magnetic moments exhibit opposite trends in both forms. For [26] the normal trend is followed with the orbital magnetic moment increasing with increasing ring quantum number. For [28] in contrast, the higher orbitals have a lower moment. In the Michl treatment of the perimeter model, it is emphasized that the actual ring currents are based on hopping between atomic orbitals on neighbouring sites, rather than on the momentum of circular waves [12]. Undoubtedly in the Möbius ring the conjugacy path is hindered by the twist, which reduces the hopping integrals.

According to the Michl theory, the Möbius system could be characterized as a *hard-negative* chromophore: this refers to a relatively large splitting of the LUMO, as compared to a very small splitting of the HOMO [14]. In this scheme the MCD is controlled by the hole contribution of the orbital levels from which the excitation starts, rather than by the electron contribution from the arrival levels. The corresponding B parameters then point to an inverted Q-band region. This argument was discussed by Sankar et al. as a possible explanation for the sign inversion. The results in Table 2 do not support this claim. Indeed the configurational composition of the excited states is quite close to the standard composition of the four-orbital model, with almost equal weights of the four-orbital transitions. Clearly the splitting of the LUMO is much smaller than the total excitation energy, and therefore does not affect the excited state composition to a significant extent. As we have pointed out the inversion must rather be attributed to the decrease of angular momentum in the LUMO levels, as compared to the HOMO. The sign anomaly of the very weak Q-band in the Möbius system cannot be explained on similar grounds, since there is no doubt that the L -moments remain large and positive. The MCD spectrum in this region rather must be based on magnetic interactions between the extremely weak Q-band and the strong B-band.

In summary, our theoretical analysis confirms that the cyclic polyene model can successfully be applied to rings with a Möbius topology. The CASCI method based on Kohn-Sham orbitals provides satisfactory estimates of magnetic transition dipoles, in line with our previous treatment of the MCD spectra of subporphyrins [4]. The calculations further show that the twisted conformation reduces the hopping integrals which sustain the conjugation path.

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