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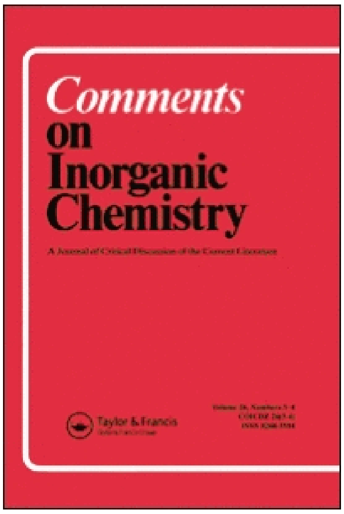

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Robust Chiral Nanostructures: Global Chirality in Supramolecules Constructed from Enantiopure Ruthenium(II) Trisdiimine Building Blocks

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Robust Chiral Nanostructures: Global Chirality in Supramolecules Constructed from Enantiopure Ruthenium(II) Trisdiimine Building Blocks

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One hallmark of supramolecular chemistry is the spatial organization of the individual components with respect to one another over nanoscopic distances. Frequently, coordination complexes play an important role in such systems, however, few are robust or inert enough to withstand a significant amount of physical or chemical manipulation. One exception is supramolecular structures constructed from enantiomerically pure [Ru(phenanthroline)$_3$]$^{2+}$ complexes. When bridged by rigid, planar aromatic tpphz ligands (tpphz = tetrapyrido[3,2-a:2',3'-c:3'',2''-h:2'',3''j]phenazine), these complexes form robust, structurally rigid and well-defined, nanoscopic complexes. A series of enantiomerically and diastereomerically pure ruthenium(II) dimers, tetramers, hexamers, decamers and linear polymers have been prepared using a stereospecific synthetic strategy involving the coupling reaction between peripheral ortho-diamine and orthoquinone groups. These structures show spatial organization over nanoscopic distances with diameters ranging from 1.6 nm to over 5.0 nm. Due to the overall rigidity, the global structure of these molecules is easily modeled and shown to differ dramatically for different diastereomers. Most

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importantly, this system presents a synthetic approach to tailorable, robust and even chiral nanoscopic structures which exhibit unique physical properties and may serve as platforms for even larger mesoscopic architectures. Because of the unique kind stereoisomerism present in these topologically different diastereomers, the term atopomers is introduced to describe their stereochemistry. These structures also show a global chirality or chiral tertiary structure which is classified by the stereochemical descriptors **P**, **M** and **T**, as defined herein.

Keywords: *chirality; topochimistry; Stereochemistry; ruthenium; polypryudyl ligands; supramolecular atopomer*

INTRODUCTION

The ability to precisely define the global structure of nanoscopic-sized molecules or assemblies is one of the most challenging issues in the emerging fields of nanochemistry and nanotechnology.[1,2] From the study of biological systems, we observe that structures such as proteins and DNA are not only possible but essential for life processes and that such magnificent architectures with unique secondary, tertiary and even quaternary structural complexity can be constructed from a relatively simple set of building blocks. A large part of the current field of supramolecular chemistry is devoted to discovering the 'rules' that dictate the self-assembly of relatively simple building blocks into well-defined nanoscopic structures and how to rationally design increasingly complex nanoscopic molecules using these rules.[2,3] Recent advances in the fields of supramolecular and dendrimer chemistry, now lead us to believe that large, spatially well-defined molecules can be rationally designed and directly synthesized in the lab. While this field is still in it infancy, it is through such developments that the principles needed to construct working molecular machines or devices will likely occur.

Currently, most examples of spatially well-defined nanoscopic molecules, such as dendrimers[4–6], helicates,[1,7–9] and various rings, squares and boxes[1,10,11], rely on coordination complexes as an essential structural component. One of the most common structural motifs is the octahedral coordination of a transition metal by three bidentate ligands to form a D_3 symmetric propeller type complex (e.g. $[\mathrm{M(catechol)_3}]^{z-}$, $[\mathrm{M(diimine)_3}]^{z+}$ and $[\mathrm{M(oxalato)_3}]^{z-}$complexes shown in Figure 1). This structural motif is somewhat unique in that it has relatively high symmetry for a chiral center (D_3 symmetry). The incorporation of such units into supramolecular structures thereby offers a means to incorporate a preferred chirality into the local structure, which, in turn, can direct the global topology and chirality of the resulting suprastructures. Indeed, many supramolecular structures incorporating trischelated metal ions exhibit a global chiral structure[12] and several have even been prepared in enantiopure form through the use of chiral ligands.[7,13,14]

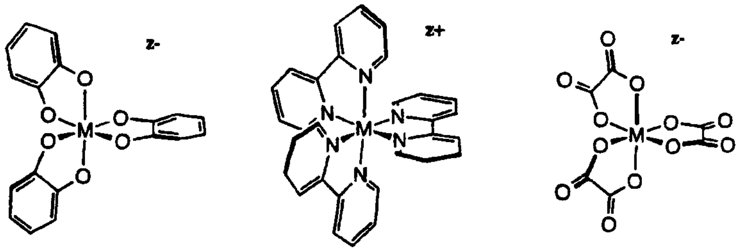


FIGURE 1 Structure of some common chiral tris-chelate octahedral metal comlexes

The ability to dictate the local chirality of the transition metal complex depends largely on the kinetic stability of the complex. Complexes which are kinetically labile, racemize quickly in solution. By using chiral ligands, the equilibrium can be shifted to favor one enantiomer and, in fact, the presence of multiple chiral centers can lead to cooperative formation of a particular global structure (e.g. the helicates).[9] The formation of these structures is under thermodynamic control. On the other hand, kinetically inert complexes, such as $[Ru(diimine)_3]^{2+}$, are much slower to racemize and structures incorporating multiple $[Ru(diimine)_3]^{2+}$ units do not equilibrate to form the most thermodynamically favored structure. Instead, these units can be treated as chiral synthons with a fixed handedness. The synthesis of supramolecular structures from such synthons provides another powerful way to direct the global topology and chirality of the product.

We shall focus on the use of $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ type complexes as building blocks for supramolecular syntheses. These complexes have been studied extensively both alone and in multi-nuclear structures (dendrimers, oligomers and polymers) because they exhibit interesting and potentially exploitable photophysical and electronic properties. They are substitutionally-inert and very robust which means that structures assembled from such units are typically quite stable under a variety of experimental conditions. This stability also means that the chirality of these units is effectively fixed once formed and that the chirality of supramolecular assemblies constructed from these units may be directed by controlling this variable. Much of our early work was directed towards the development of stereospecific syntheses of assemblies containing multiple $[Ru(diimine)_3]^{2+}$ units.[15]

Preset Chiral Synthon for Supramolecular Syntheses

The formation of diastereomers upon linking multiple $[Ru(diimine)_3]^{2+}$ units was recognized as one significant drawback of this synthetic system because of the difficulty of performing such reactions stereoselectively. Even now, there are only a few viable routes for the syntheses of enantiomerically pure (ep) and diastereomerically pure (dp) multimetallic assemblies. Von Zelewsky and coworkers[16] have shown it is possible to stereoselectively form a given enantiomer through the use of chiragens (chiral bpy ligands). This technique has been successfully extended to multinuclear assemblies of ruthenium(II) and has the advantage that the stereochemistry at the metal site is predetermined by the ligand chirality.[17,18] Other stereospecific strategies for multinuclear assemblies of ruthenium(II) have required the use of ep monomers as precursors. The groups of Keene[19,20], von Zewlewsky[21,22] and Lehn[23–25] have shown that enantiopure complexes with two labile ligands, such as *cis*-$[(phen)_2RuL_2]^{2+}$ or *cis*-$[(bpy)_2RuL_2]^{2+}$ (where L is either py or CO) can undergo a stereospecific ligand-displacement reaction with multitopic ligands to form ep and dp dimers and trimers of the type shown in Figure 2.

In order to avoid bond breaking and formation reactions at the metal stereocenter, the groups of Tor[26] and Lehn[23] have each explored the use preresolved trisdiimineruthenium(II) complexes as chiral building blocks which are linked by organic ethynyl or phenylene functional groups along the ligand periphery. In order to utilize the full symmetry of the building block and to restrict rotational and conformational motion, we pursued a coupling strategy as shown in Scheme 1. The peripheral dione and diamine functions undergo a high yield (ca. 90%) condensation reaction to form a rigid tpphz bridge between mono-

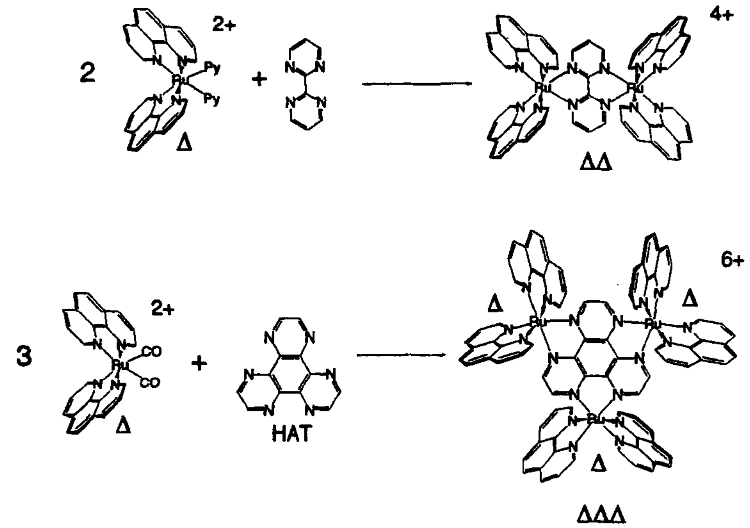
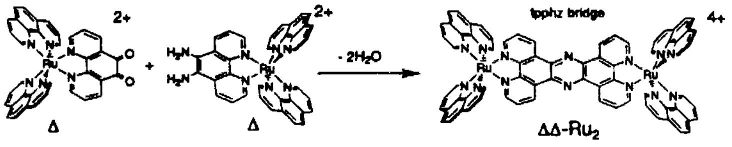


FIGURE 2 Stereospecific ligand displacement reactions for the construction of ep and dp polynuclear complexes

mers.[27] By symmetrically substituting the 1,10-phenanthroline-5,6-dione (phendione) and 1,10-phenanthroline-5,6-diamine (phendiamine) ligands, bridges off all three axes can be introduced without formation of *mer* and *fac* regioisomers in the product, as shown in the synthesis of the D_3 symmetric tetranuclear ruthenium complexes in Scheme 2.[28] The planar aromatic tpphz bridge also serves to fix the Ru – Ru distance and rigidly lock the product into one specific geometry. The result is that even giant structures such as $\mathbf{Ru_4}$ (diameter of ca. 32 Å) are conformationally rigid (notwithstanding slight bending and twisting motions about the metals and bridges).

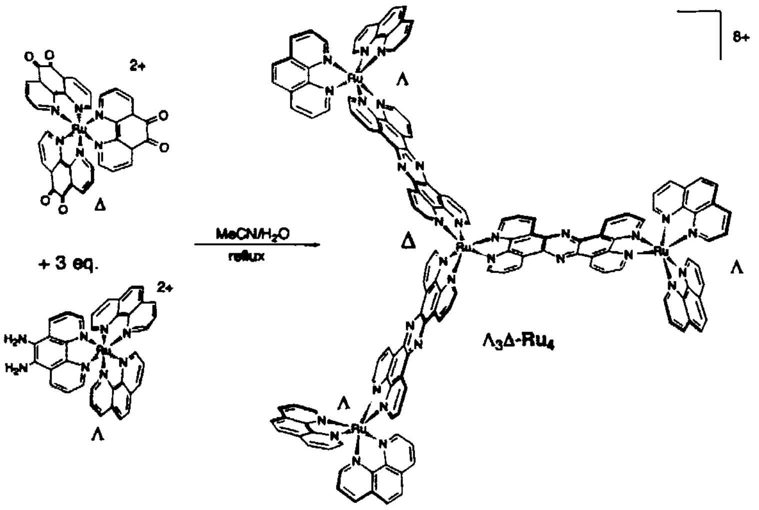
DENDRIMERS AND POLYMERS

If we view the topology of the ep and dp dimers ($\mathbf{Ru_2}$) and tetramers ($\mathbf{Ru_4}$) strictly with respect to the connectivity and orientation of the



SCHEME 1 Stereospecific synthesis of a rigid, ep and dp ruthenium dimer using a ligand based coupling reaction

ruthenium ions with respect to each other, we could say that all the dimers are topologically similar and as well as the tetramers. The three dimers ($\Delta\Delta$-$\mathbf{Ru_2}$, $\Lambda\Lambda$-$\mathbf{Ru_2}$, and $\Delta\Lambda$-$\mathbf{Ru_2}$) forming a simple linear fragment and the four tetramers($\Delta_3\Delta$-$\mathbf{Ru_4}$, $\Lambda_3\Lambda$-$\mathbf{Ru_4}$, $\Lambda_3\Delta$-$\mathbf{Ru_4}$, $\Delta_3\Lambda$-$\mathbf{Ru_4}$) forming a trigonal planar arrangement of Ru ions. This is no longer true when we construct higher order dendrimers or polymers.



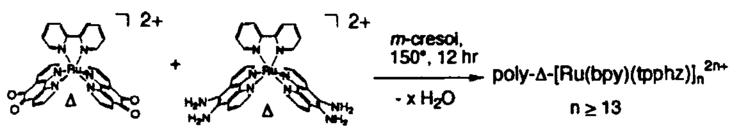
SCHEME 2 Formation of $\Lambda_3\Delta$-$\mathbf{Ru_4}$ tetramer from substitutionally inert, chiral precursors

The simplest case in which we observe topological isomerism (in this case locked torsional isomers) is when consider a 'linear' chain of four

$[Ru(diimine)_3]^{2+}$ centers bridged by tpphz ligand, as shown in Figure 3. The topology of the resulting chain will depend on the stereochemical make-up of the individual units and in particular on the central two Ru sites. In total, four "locked" torsional isomers are possible for this linear tetramer, two for the meso (Δ-Ru(2)and Λ-Ru(3)) and two for the homochiral structures (Δ-Ru(2)and Δ-Ru(3); (Λ-Ru(2)and Λ-Ru(3)). As shown in the Newman projection in Figure 4, every 4 metal unit can exhibit a form of *cis* and *trans* stereochemistry of which the torsional angle (Θ for Ru(1)-Ru(2)-Ru(3)-Ru(4)) is dependent on the chirality of the central two (Ru(2)-Ru(3)) metal centers. The Newman projections for the meso (Figure 4, left) and homochiral (Fig. 4, right) polymers are viewed down the Ru(2)-Ru(3) axis (with the intervening tpphz parallel with the horizontal axis). The frontmost two chelating rings on Ru(2) and back two chelating rings on Ru(3) are visible. As can be seen the front and back chelate rings eclipse one another for the meso structure (local C_{2h} symmetry) and are staggered for the homochiral structures (local D_2 symmetry). If the chain is oriented such that the link from Ru(1) comes in along the **b** quadrant (indicated by a dark arrow), we can denote each torsional isomer by which quadrants the entering and leaving tpphz ligands are in (quadrants labeled in Figure 4). For the meso structure, only the *cis*-(**b**,**b**)-isomer and *trans*-(**b**,**d**)-isomer, which have torsional angels (Θ) of 0° and 180° respectively, are allowed. The descriptors, *cis* and *trans* are used with their usual meaning for a chain of four coplanar objects (in this case Ru ions). The homochiral chains, however, have different torsional angles for the *syn* -(**b**,**a**)-isomer (Θ= 72°) and *anti*-(**b**,**c**)-isomer (Θ = 108°) which will dramatically affect the overall topology. These torsional angles were determined from molecular modeling of related dendrimer systems in conjunction with crystallographic data for Λ-$[Ru(phen)_3][PF_6]_2$ [38]and the dimer ΔΛ-$[(bpy)_2Ru(tpphz)Ru(bpy)_2]$ $[NO_3]_4$.[11] Here we use descriptors *syn* and *anti* to describe these non-planar torsional isomers and determine the usage relative to the central horizontal tpphz plane. The *syn* isomer has both Ru(1) and Ru(4) on the same side of this tpphz plane whereas the *anti* isomer has them on opposite sides. Thus we can observe that the stereochemical sequence in this simple linear tetramer can have a dramatic effect on the topology of the chain – even if viewed simply with respect to the Ru ion connectivity and orientation.

While we have not made these linear tetramers, we have made linear coordination polymers[29] containing at least 13 such chiral centers

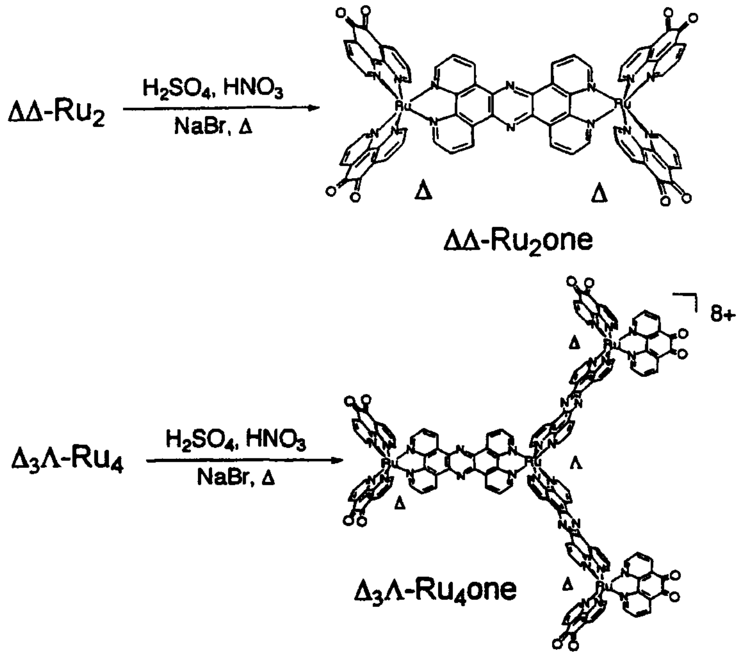
($P_n = 13$) using the condensation reaction of enantiopure monomers with two derivatized phenanthrolines, as shown in Scheme 3. Both homochiral and meso type polymers were prepared and characterized by NMR and CD. From the above considerations, we can predict that the meso polymer has a zig-zag structure containing only *cis* and *trans* torsional isomers and therefore a structure in which all the Ru atoms are approximately coplanar. On the other hand, the homochiral polymers will form random coil structures due to the presence of only *syn* and *anti* torsional isomers. Currently, the use of enantiopure monomers only permits partial control of the main chain topology for these polymers, nonetheless the point can be made that stereochemical control in such a rigid system can have profound effects on the global topology of the resulting multinuclear assembly.



SCHEME 3 Condensation polymerization of chiral monomers to give a rigid chiral coordination polymer

The formation of rigid torsional isomers has an even more pronounced effect on the global topology of larger rigid dendritic structures. Both the dimer **Ru_2**and tetramer **Ru_4** could be modified with peripheral dione functions as shown in scheme 4. While this oxidation involves harsh reaction conditions, we have demonstrated through model studies that the stereochemistry of the starting material is retained.[30] The condensation reaction of the appropriate enantiomer of **Ru_2-one** and **Ru_4-one** with excess Λ or Δ-$[Ru(phen)_2(phendiamine)]^{2+}$ gave the desired hexameric (**Ru_6**) and decameric (**Ru_{10}**) structures shown in Figure 5. The hexamers and decamers were characterized by NMR nd ESI-MS in addition to circular dichroism and absorption spectroscopy. They are truly nanoscopic and, like their smaller predecessors, are conformationally rigid molecules.

For the hexamers, four diastereomers were prepared, the heterochiral isomers, $\Delta_4\Lambda_2$-**Ru_6** and $\Lambda_4\Delta_2$-**Ru_6** as well as the homochiral hexamers,



SCHEME 4 Selective oxidation of terminal 1,10-phenanthrolines to 1,10-phenanthroline-5,6-dione on dimeric and tetrameric structures

$\Lambda_4\Lambda_2$-**Ru**$_6$ and all $\Delta_4\Delta_2$-**Ru**$_6$.[31] These complexes have diameters estimated at 4.6 nm and retain the D_2 symmetry of the core molecule. A space-filling model of $\Delta_4\Lambda_2$-**Ru**$_6$ is shown in Figure 6. As can be seen, the hexamer exhibits a global twist when viewed down the principal C_2 axis (the central Ru-tpphz-Ru axis). As depicted by the ball and stick picture, the connectivity and orientation of the Ru atoms defines a pair of skewed lines which can be assigned an overall or global "left-handedness". We use the stereochemical descriptors **P** (for plus or clockwise helicity) and **M**(for minus or counterclockwise helicity), as in **M**($\Lambda_4\Lambda_2$)-**Ru**$_6$ to describe the global chirality in addition to the conventional Δ and Λ for the local stereochemistry. We note that the diastereomer ($\Delta_4\Lambda_2$)-**Ru**$_6$ has the same descriptor **M** while the other two are

$P(\Delta_4\Delta_2)$-**Ru**$_6$ and $P(\Lambda_4\Delta_2)$-**Ru**$_6$. We observe that all four are topologically very similar. If the local stereochemistry is ignored and we simply observe the connectivity and spatial organization of the Ru atoms, we may say that all the **P** and all the **M** hexamers are enantiomorphic in a global sense.

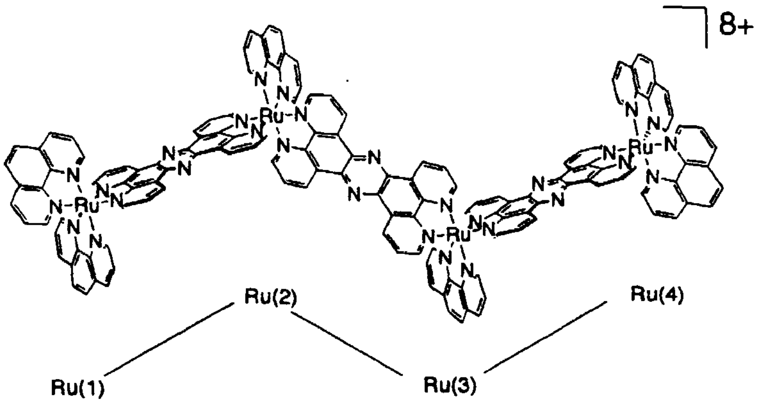


FIGURE 3 Smallest fragment of a linear tpphz bridged oligomer displaying "locked" torsional isomerism dependent of the absolute stereochemistry of Ru(2) and Ru(3)

It is important to clarify our use of the current stereochemical descriptors for objects with helical chirality. The descriptors **P** and **M** are commonly used to describe helical chirality in for molecules containing a chiral axis.[32,33] For many organic molecules containing a chiral axis, such as chiral allenes, spiranes and ortho-substituted biphenyls, the helicity is determined by aligning the chiral axis along the helical axis and establishing a priority order for the substituents; **P** and **M** are assigned as shown in Fig 7 (I). **P** describes a right-handed helix or a helix propagating in a clockwise fashion about this axis and **M** describes the mirror image structure. In this case the angle between the two lines (front and back) are unimportant. For our D_2 symmetric hexameric structures, there is nothing to differentiate or prioritize the peripheral Ru sites, however, they do form a pair of skewed lines as described before (Figure 7). When viewed down the highest order C_2 axis (containing both central Ru atoms), the helicity of the complex can be assigned as shown in Figure 7(II). However, an alternative and the IUPAC recommended assignment of helicity[34,35] is shown in Figure 7(III). In this case, one of the two skewed lines is chosen as the helix axis and the other line is viewed as being tangent to an imaginary helical coil propagating about this axis. Note that the two pictures on the left (Figure 7; II and III) and the two on the right (Figure 7; II and III) are the same. As can be seen, this change in viewpoint leads to an assignment of helicity that is opposite to that obtained when the molecule is aligned along the highest symmetry axis. While former method (Figure 7 (II)) has the obvious relationship with the system used for organic molecules with a chiral axis (both align the chiral axis with the helix axis), the latter is well-established in inorganic chemistry[36]and is used for the assignment of the global helicity for the hexamers.

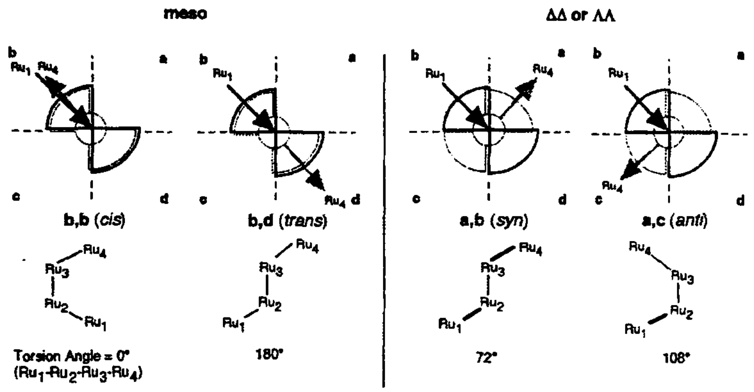


FIGURE 4 Newman projections of the 'linear' tetramer with a central (Ru(2)-Ru(3)) meso or homochiral configuration

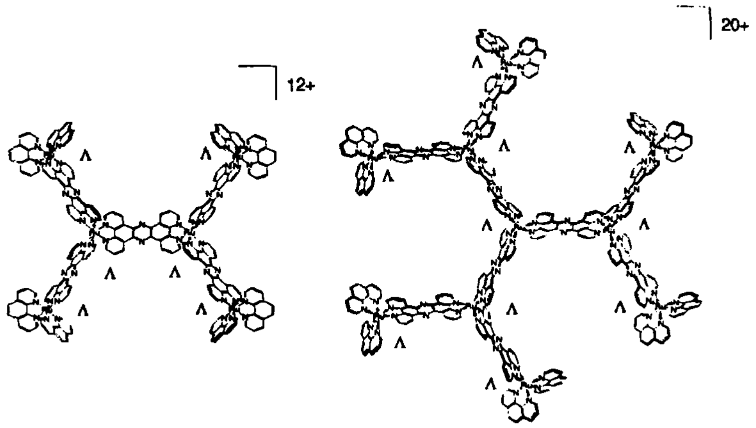
GLOBAL TOPOLOGY OF DECAMERIC STRUCTURES

The most interesting global stereochemistry arises in our decameric dendrimers. A total of four isomeric decamers, $\Lambda_6\Lambda_3\Lambda$-**Ru$_{10}$**, $\Lambda_6\Delta_3\Lambda$-**Ru$_{10}$**, $\Delta_6\Delta_3\Delta$-**Ru$_{10}$** and $\Delta_6\Lambda_3\Delta$-**Ru$_{10}$**, have been prepared,[31,37] two of which are shown in Figure 8. All of the decamers have diameters of ca. 5.4 nm and still retain the D_3 point group symmetry of the core.

The structures of $\Lambda_6\Delta_3\Lambda$-$\mathbf{Ru_{10}}$ and $\Lambda_6\Lambda_3\Lambda$-$\mathbf{Ru_{10}}$, have been determined by molecular modeling (Spartan, MM2) using the crystallographic coordinates for the $[\mathrm{Ru(phen)_3}]^{2+}$ unit[38] to give accurate metal-ligand bond lengths and angles. The two isomers differ only in the stereochemistry at three dendritic sites, however as can be seen, this small change has a dramatic effect on the overall topology. When viewed from the central Ru core, each arm consists of a plane of four ruthenium centers. For $\Lambda_6\Lambda_3\Lambda$-$\mathbf{Ru_{10}}$, the pitch angle of this plane relative to the molecular C_3 axis is ~18°. For $\Lambda_6\Delta_3\Lambda$-$\mathbf{Ru_{10}}$ this pitch angle is 90° resulting in a flat disk-like structure. The macroscopic pitch angle is a direct consequence of the local 36° pitch angle relative to the C_3 axis found for the $[\mathrm{Ru(phen)_3}]^{2+}$ synthons.[38] For the 'flat' isomer, the all 10 Ru atoms lie in the same plane whereas the structure on the right can be viewed as a central 4-metal planar unit with the outermost Ru sites above and below this plane resulting in a massive *right-handed* propeller structure. For the flat structure, the central and adjacent metal sites have the opposite handedness. As was shown in Figure 4, this meso configuration leads to *cis* or *trans* isomers in a linear complex. Here since both the *cis* and *trans* sites are occupied, a planar disk-like structure results. For $\Lambda_6\Lambda_3\Lambda$-$\mathbf{Ru_{10}}$, the $\Lambda\Lambda$ configuration of the central and adjacent Ru sites leads to the *syn* and *anti* torsional isomerism observed in Fig 4. Since both *syn* and *anti* isomers are present, the torsional angle for the pitch of this arm is defined as the 72° acute angle relative to the central 4-metal plane.

Another, perhaps simpler, analysis would be the structural analogue of gluing of one blade of a left or right-handed (three bladed) propeller to each of the blades of a central left-handed (three-bladed) propeller. The propeller twist can either add or cancel. The propeller pitch angle for Λ-$[\mathrm{Ru(phen)_3}][\mathrm{PF_6}]_2$ is 54° relative to its molecular C_3 axis or 36° relative to the plane perpendicular to the C_3 axis.[38] Since these angles are not 45°, inspection of $\Lambda_6\Lambda_3\Lambda$-$\mathbf{Ru_{10}}$ reveals that the plane defined by any four metal arm is tilted by 18° with respect to the molecular C_3 axis to give a massive right-handed helical twist to the structure. However for $\Lambda_6\Delta_3\Lambda$-$\mathbf{Ru_{10}}$, the pitch angles (irrespective of what they are) cancel out to give a flat disk like structure. Thus in these dendrimers, we observe a specific global topology and chirality as a function of stereochemical composition.

In order to assign a global stereochemical descriptor to these decamers, we can view each dendrimer as a simple stick figure (see Figure 9 –



$\Lambda_4\Lambda_2$-Ru$_6$

$\Lambda_6\Lambda_3\Lambda$-Ru$_{10}$

FIGURE 5 Chemdraw representations of one of the hexanuclear (**Ru$_6$**) and dendritic decanuclear (**Ru$_{10}$**) structures

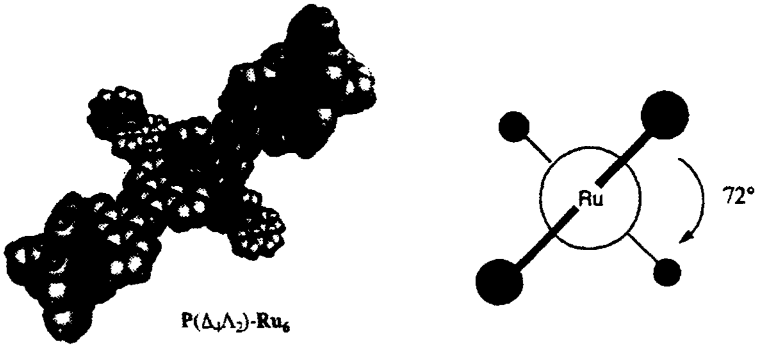


FIGURE 6 Spacefilling model (left) of the hexanuclear structure, **P($\Delta_4\Lambda_2$)-Ru$_6$**, with a simplified ball (Ru complex) and stick (tpphz bridge) representation (right)

where each line represents a tpphz bridge and each solid circle a Ru metal center) indicating the connectivity and spatial organization of the Ru centers. The decamer on the left could be described as "achiral" or planar with respect to global helicity because it has a skeleton structure in which all 10 rutheniums lie in the same plane (D_{3h} symmetry) whereas the decamer on the left has a global right-handed twist (D_3 symmetry). Using this picture, we describe the global topology for the 'planar' decamer with a **T**. In this case, the **T** describes a situation in which the torsional angle for any chain of 4 Ru atoms comes to either 0° or 180°. Here, the use of **T** notation is adopted from Brewster's work describing the chirality or lack thereof in twisted chains of atoms.[39] These global stereochemical descriptors (**P**, **M** and **T**) are useful in that we observe that they serve to group diastereomers which exhibit topologically similar structures. For example, structures with **P** and **M** global descriptors can be described as globally enantiomorphic (though not strictly for diastereomers such as **P**($\Lambda_6\Lambda_3\Lambda$)-$\mathbf{Ru}_{10}$ and **P**($\Delta_6\Lambda_3\Lambda$)-$\mathbf{Ru}_{10}$) and all the **T** structures (($\Lambda_6\Delta_3\Lambda$)-$\mathbf{Ru}_{10}$, ($\Delta_6\Lambda_3\Delta$)-$\mathbf{Ru}_{10}$ ($\Delta_6\Delta_3\Lambda$)-$\mathbf{Ru}_{10}$, ($\Lambda_6\Lambda_3\Delta$)-$\mathbf{Ru}_{10}$) can be described as 'achiral' and 'isomorphic' with each other, and obviously very different from the **P** and **M** structures.

ATOPOMERS: A NEW SUBCLASS OF DIASTEREOMERS

We have shown that it is possible to prepare rigid diastereomers which have similar or related global topologies whereas other diastereomers have significantly different topologies. There is some difficulty in describing the exact kind of isomerism that exhibited by such complexes. Although the term diastereomers is accurate, it does not relate any information regarding the huge topological differences in structure nor classify certain isomers as being topologically similar. Other more specific terms such as topoisomers, atroposiomers and torsional isomers are not technically correct for these structures either.[32] Topoisomers by definition require bond breakage to interconvert isomers.[36] As may be imagined, the various structures presented herein may be interconverted upon racemization by either a Bailor twist, a Ray-Dutt twist [36,40], or via bond breakage and reformation. The former two do not invoke bond breakage and, although neither racemization mechanism is observed to occur in this system under standard laboratory conditions, the possibility of such a transformation rules out the term topoisomers. In a similar manner terms, such as atropisomers and torsional isomers are, by definition, inappropriate.[32]

We propose that the term atopomers be used to describe these topologically rigid diastereomers. Topomers by definition are two structures

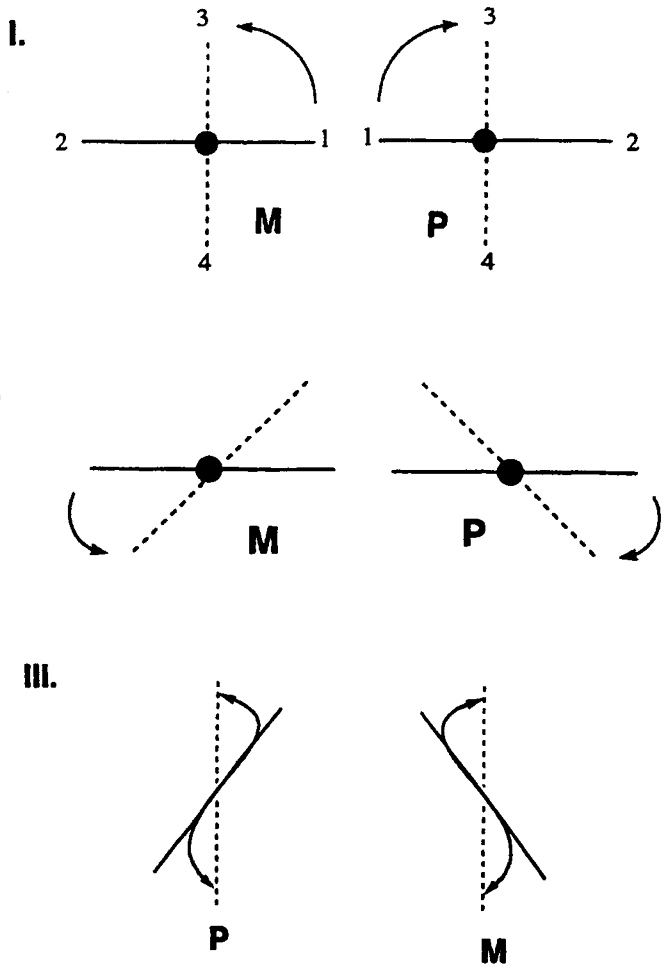


FIGURE 7 Assignment of P or M stereochemical descriptors of axial chirality for I. orthogonal lines; II. skewed lines when viewed down the principle C_2axis; and III. skewed lines when one line is parallel with the helical axis

that are superimposable but have undergone exchange of two or more ligands.[32] Since exchange of just two imine nitrogen's at the central Ru

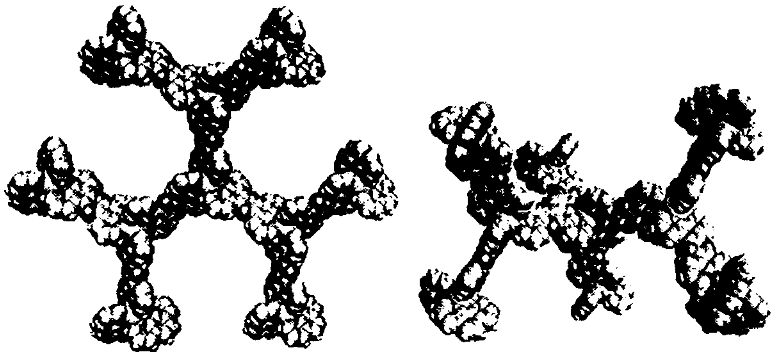


FIGURE 8 Spacefilling models of the rigid dendritic decamers, $\mathbf{T}(\Lambda_6\Delta_3\Lambda)$-$\mathbf{Ru_{10}}$ (left), and $\mathbf{P}(\Lambda_4\Lambda_2\Lambda)$-$\mathbf{Ru_{10}}$ (right)

site can change the stereochemistry at that site, a structure such as $\mathbf{P}(\Lambda_6\Lambda_3\Lambda$-$\mathbf{Ru_{10}})$ and $\mathbf{T}(\Lambda_6\Lambda_3\Delta$-$\mathbf{Ru_{10}})$ may be interconverted. In this case, since two identical groups are exchanged and the products are *not* superimposable we call them atopomers. We realize that this is a new term and definition but, given the lack of a better term, choose to use it. We observe that the name ***atopomer*** seems oddly appropriate to describe these rigid *topologically-interesting* molecules. We will also use the global stereochemical descriptors (**P**, **M** and **T**), when applicable, to classify these atopomers.[39]

The dramatically differing global topologies of the **P**, **M**, and **T** decamers, surprisingly, did not lead to any readily discernable features in the UV-Vis or CD spectra that unambiguously can be attributed to a particular atopomer. The absorption, luminescence and circular dichroism spectral data for the various ruthenium complexes are collected in Table I. Figure 10 shows a plot of the magnitude extinction coefficient in the MLCT region (λ=480 nm, MeCN) as a function of the number of ruthenium centers in the structure. The linear fit shows that the chromophores are largely independent of one another. As shown in Figure 11, we also do not observe any readily discernible features in the CD that unambiguously can be attributed to either isomer. On the contrary, the magnitude of the CD in the MLCT region (420–480 nm) is approximately proportional to the number of individual chromophores in enantiomeric excess (ee) within each structure. For the homochiral isomer, $\mathbf{P}(\Lambda_6\Lambda_3\Lambda)$-$\mathbf{Ru_{10}}$, an intense molar CD of +178 (477 nm, MeCN) is observed, which is roughly a 10-fold increase over molar CD of Λ-$[Ru(phen)_3]^{2+}$ (+21 at 471 nm in MeCN). **T($\Lambda_6\Delta_3\Lambda$)-Ru_{10}** gives a molar CD of +76 at 464 nm corresponding approximately four times of molar CD of Λ-$[Ru(phen)_3]^{2+}$ chromophores in enantiomeric excess. The lack of CD features related to the global chirality in P($\Lambda_6\Lambda_3\Lambda$)-**$Ru_{10}$** can be explained due to weak electronic interaction between chromophores.

TABLE I Absorption, circular dichroism properties of each generation of dendrimers in MeCN deaerated solution at 25°C

	Absorption	*CD*
	λ_{max} nm (ε, $M^{-1}cm^{-1}$)^a	*$\lambda_{min/max}$ ^{*b}, (Mol. CD)*
mononuclear complexes		
Λ-$[Ru(phen)_3]^{2+}$	442 (19200)	467 (+21)
Λ-$[(phen)_2Ru(phendione)]^{2+}$	434 (14800)	459 (+13)
Λ-$[(phen)_2Ru(phendiamine)]^{2+}$	455 sh (15200)	470 (+17)
Λ-$[Ru(phendione)_3]^{2+}$	417 (14700)	453 (+10)
dinuclear complexes		
$\Delta\Delta$-Ru_2	439 (36500)	470 (-36)
$\Lambda\Lambda$-Ru_2	438 (35500)	470 (+36)
$\Lambda\Delta$-Ru_2	439 (38100)	-
tetranuclear complexes		
$\Delta_3\Delta$-Ru_4	439 (86000)	476 (-73)
$\Lambda_3\Delta$-Ru_4	439 (78000)	466 (+36)
$\Delta_3\Lambda$-Ru_4	441 (76000)	466 (-38)
$\Lambda_3\Lambda$-Ru_4	439 (85000)	475 (+68)
hexanuclear complexes		
$\Delta_4\Delta_2$-Ru_6	440 (140,000)	475 (-104)
$\Lambda_4\Lambda_2$-Ru_6	440 (135,000)	477 (+117)
$\Lambda_4\Delta_2$-Ru_6	441 (136,000)	464 (+45)
$\Delta_4\Lambda_2$-Ru_4	441 (138,000)	459 (-44)
decanuclear complexes		
$\Delta_6\Delta_3\Delta$-Ru_{10}	440 (208,000)	483 (-183)
$\Lambda_6\Lambda_3\Lambda$-$Ru_{10}$	440 (205,000)	477 (+178)
$\Lambda_6\Delta_3\Lambda$-Ru_{10}	441 (220,000)	464 (+76)
$\Delta_6\Lambda_3\Delta$-Ru_{10}	441 (225,000)	467 (-75)

a. Only the lowest energy maximum or shoulder is given.

b. λmax or min for the lowest energy transition.

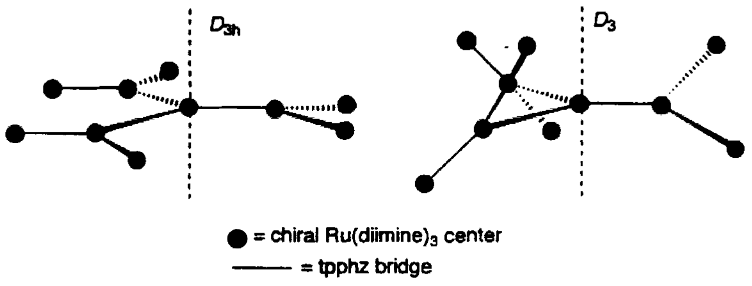


FIGURE 9 Connectivity and orientation of Ru stereocenters for decamers with **T** (left) and **P** (right) global topology

Significantly, the differing topologies for $\mathrm{T}(\Lambda_6\Delta_3\Lambda)\text{-}\mathbf{Ru}_{10}$ and $\mathbf{P}(\Lambda_6\Lambda_3\Lambda)\text{-}\mathbf{Ru}_{10}$ do affect the colloidal properties as measured by electric birefringence. Campagna and coworkers have shown previously that related metallodendrimers are colloidal in dilute acetonitrile solution.[41] Dynamic light scattering experiments show that both $\mathrm{T}(\Lambda_6\Delta_3\Lambda)\text{-}\mathbf{Ru}_{10}$ and $\mathbf{P}(\Lambda_6\Lambda_3\Lambda)\text{-}\mathbf{Ru}_{10}$ exhibit polydisperse aggregation phenomena in acetonitrile (as the hexafluorophosphate salt) and water (as the chloride salt). While no distinction between diastereomers could be observed in the light scattering experiment, both the amplitude and relaxation time for the forward and backwards birefringence signals (Figure 12) clearly show a distinct difference for the two colloids. For the **T** isomer (74 μM, Cl$^-$ salt in water), the amplitude of the birefringence is small and the corresponding decay signal is fast (in the sub micro-second range). On the other hand, for the **P** isomer (77 μM, Cl$^-$ salt in water) the amplitude of the birefringence is much larger and the decay far slower (in the milli-second range) and anomalous (full data not shown). In order to confirm that this result is a consequence of differing topology and not simply the diastereotopic nature of the complexes, $\Lambda_3\Delta\text{-}\mathbf{Ru}_4$ and $\Lambda_3\Lambda\text{-}\mathbf{Ru}_4$ were examined. These two diastereomers have globally similar molecular topologies and also form polydisperse colloids in aqueous solution. In this control, the birefringence signals were indistinguishable (both 0.22 mM, Cl$^-$ salt in water). It is apparent that under the influence of an electric field, the isotropic chiral solution of $\mathbf{P}(\Lambda_6\Lambda_3\Lambda)\text{-}\mathbf{Ru}_{10}$ becomes optically anisotropic, which is likely due to structural distortion/orientation of the aggregates in the

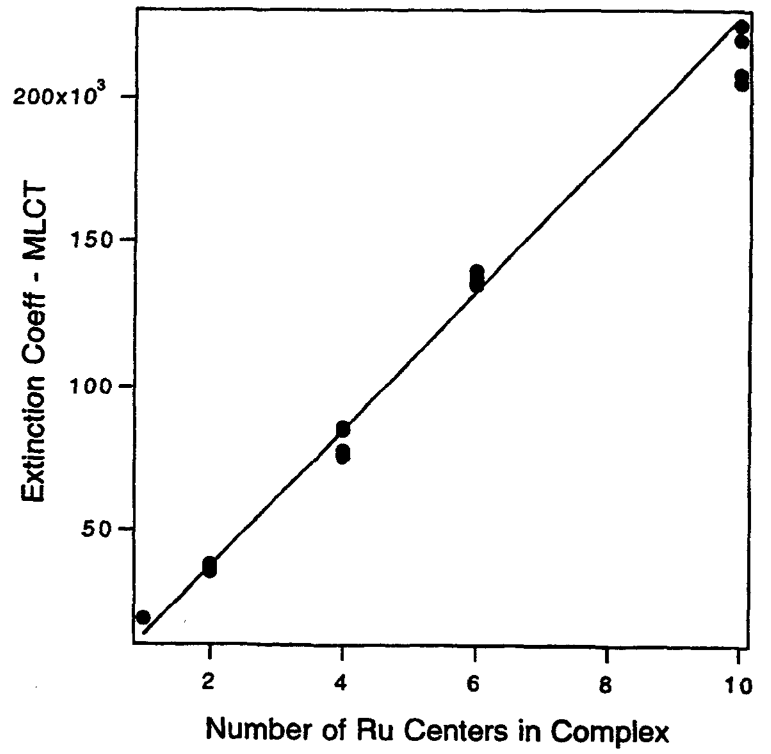


FIGURE 10 Plot of the molar extinction coefficient (ε) at 480 nm as a function of the number of ruthenium centers in the molecule

direction of the field *E*, whereas the rapid evolution of the birefringence for **T($\Lambda_6\Delta_3\Lambda$)-Ru$_{10}$** can be attributed to electronic polarization. These dramatic results show the importance of tertiary structure on the colloidal and macroscopic properties of such systems.

SUMMARY

We have described a conceptually simple yet but powerful synthetic methodology for the construction of diasteromerically and enantiomeri-

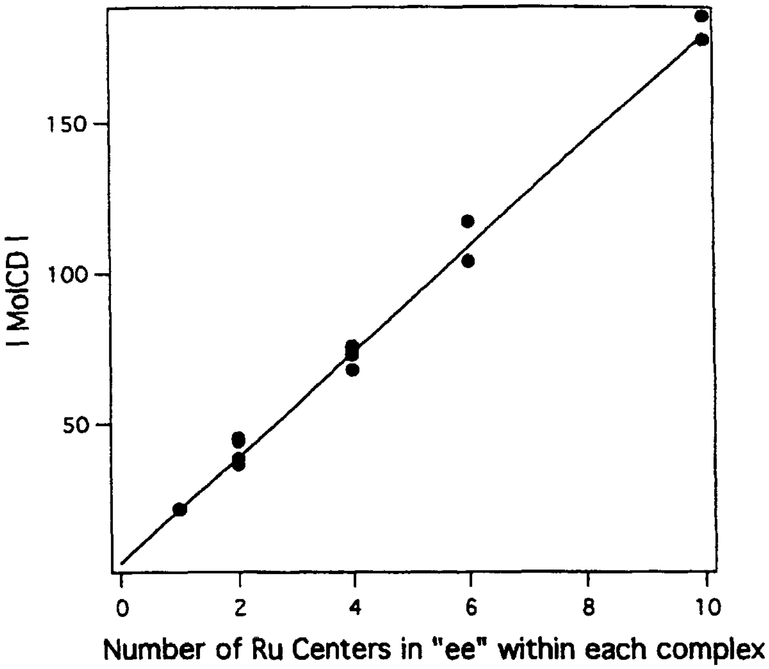


FIGURE 11 Plot of the absolute value of the molar CD at 500 nm as a function of the number of individual stereocenters in "enantiomeric excess (ee)" within a given molecule

cally pure supramolecular assemblies. The use of enantiopure $[Ru(phen)_3]^{2+}$ derivatives as the fundamental molecular building blocks for supramolecular syntheses has several distinct advantages in that the complexes are very robust chemically, readily resolved at the monomer stage, exhibit potentially useful luminescent properties, are diamagnetic and are highly symmetric. The rigid monomer structure and planar aromatic bridge formed between monomers permits the directed synthesis of topologically distinct diastereomers, many of which exhibit global chirality.

The atopomers presented herein show elements of primary, secondary, tertiary and possibly even quaternary structure in a remarkable analogy to biological structures. Here, the primary structure would be the stereo-

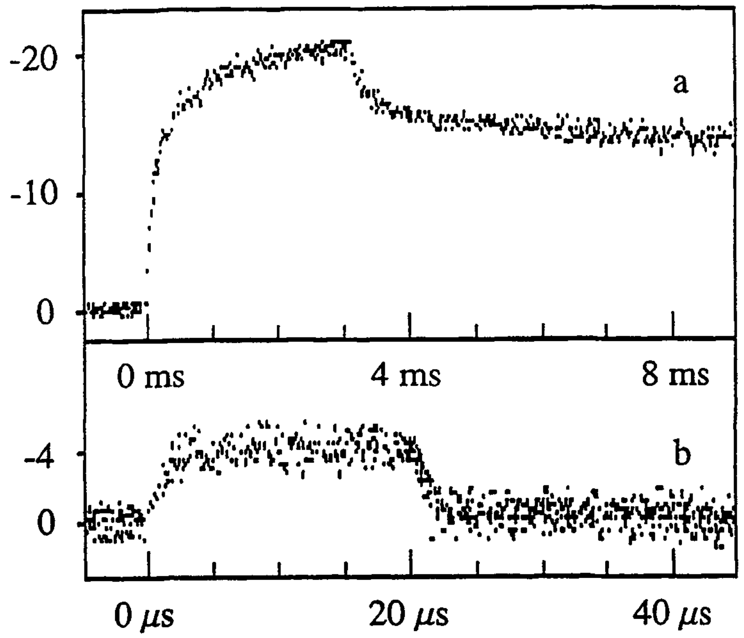


FIGURE 12 Plot of the electric field-induced birefringence signals (E= 4.8 kV/cm) of **P($\Lambda_6\Lambda_3\Lambda$)-Ru$_{10}$** (**a**: top trace, pulse length = 3 ms) and **T($\Lambda_6\Delta_3\Lambda$)-Ru$_{10}$** (**b**: bottom trace, pulse length = 20 μs). The ordinate is proportional to the transmitted light intensity

chemical sequence. Secondary structure is exemplified by the presence of 4-metal planes. Whereas three points define a plane, four need not. We observe that four metal units (one central and three peripheral) all form trigonal planar units. The global structure is analogous to the tertiary structure of a monomeric protein and the observed colloidal behavior (strong dependence of tertiary structure) suggests that specific aggregates arise in solution giving rise to quaternary structure.

We continue to explore the ramifications and uses of these structurally precise, nanoscopic molecules and to develop new ways to construct even more complex architectures. Ultimately, we aim to use such structures as nanoscopic platforms from which to organize and construct mesoscopic 'arrays' of nanomolecules.

Acknowledgements

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