Conformational changes and chiroptical switching of enantiopure bis-helicenic terpyridine upon Zn^{2+} binding

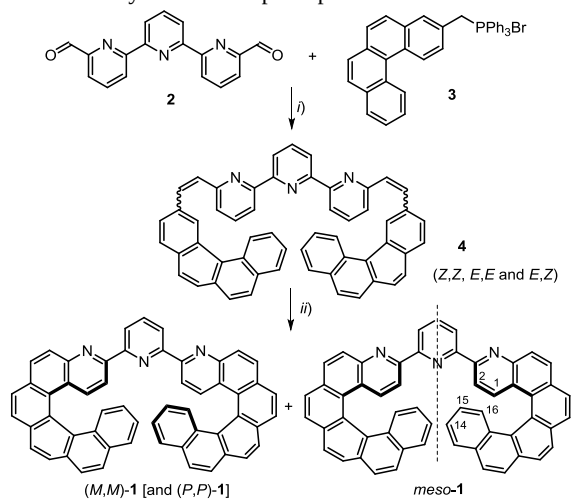
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The molecular conformation of a bis-helicenic terpyridine system is strongly modified upon binding to Zn(II) ion, a process that is accompanied by large changes in the optical and chiroptical properties. This system affords a new type of helicene-based chiroptical switching.

The contribution of chiroptical molecular switches[1] to the field of functional devices is stimulated by many potential applications such as molecular information processing, data storage, or probes for the detection of chirality.[2] Interconversion between two or more stable chiral forms can result from responses of chiral molecules to external stimuli such as heat, light, pressure, solvent, pH, change in redox potential or presence of chemicals. The response at the molecular level can be transduced to a read-out process through the effect on chiroptical activity; *e.g.*, optical rotation, electronic circular dichroism (ECD), and circularly polarized luminescence (CPL). Efficient, practicable switching between two (or more) molecular states, is based on stability, non-destructive read-out, fast response times, reproducibility and fatigue resistance. An important requirement is a large response difference between the states to ensure unambiguous read-out.

In the last decade, helicenes have appeared as attractive candidates for molecular materials and chiroptical switches due to their helical π-conjugated structure which gives rise to strong chiroptical properties such as huge optical rotation values, intense ECD spectra and significant CPL activity.[3] Examples of helicene-based chiroptical switches have been recently reviewed.[4] However, the creation of structural diversity is still necessary to develop new kinds of functions in helicene-based chiral systems and to create innovative molecular devices. In this regard, several transition-metal complexes formed from helical π-conjugated ligands have recently been shown to display unprecedented chiroptical and electronic properties that are switchable by redox or acid/base stimuli.[5] While in those examples the helical topology and integrity of the chemical backbone was maintained upon switching, constructing a scaffold in which movements can take place through geometrical and conformational changes is particularly appealing. Such conformational changes in chiral systems may lead to molecular motors with effective unidirectional motion.[2,6]

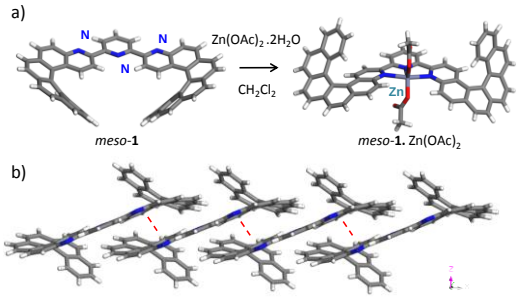
In this communication, we describe the synthesis of the first bis-helicenic terpyridine ligand (*meso*-, (*M*,*M*)- and (*P*,*P*)-**1** in Scheme 1) acting as a chiroptical switch upon reversible coordination-decoordination to zinc(II). The profound conformational changes induced lead to a multi-output read-out system, showing responses in ECD, fluorescence and CPL-activity. The (chir)optical changes accompanying the interconversion between the ligand and zinc-complexed states have been analyzed via first-principles calculations.



Scheme 1. Synthesis of bis-helicenic terpyridine **1**. *i*) *n*-BuLi, THF, r.t., 5 h, 82%; *ii*) hν, cat. I_2, toluene/THF, r.t., 7 h, 45%.

The synthesis of ligand **1** was accomplished as described in Scheme 1. First, a Wittig reaction between terpyridine bis-aldehyde **2**[7a] and (benzo[c]phenanthren-3-ylmethyl)triphenyl-phosphonium bromide **3**[7b] yielded bis-olefin **4** as a mixture of three isomers (*E*,*E* - major compound, *Z*,*Z*, and *E*,*Z*). Subsequent photo-irradiation (700 W Hg lamp) in a toluene/THF mixture at room temperature (r.t.) in the presence of catalytic iodine, furnished bis-helicene-terpyridine **1** as a statistical mixture of (*M*,*P*)-**1** (*meso*-**1**) and racemic (*P*,*P*)- and (*M*,*M*)-**1**. The structure of *meso*-**1** was confirmed by NMR spectroscopy and by X-ray diffraction studies. The ^{1}H NMR spectrum is in agreement with its C_s symmetry and displays the typical signature of [6]helicene derivatives such as for example degenerate triplets at 6.8 and 7.3 ppm corresponding to H^{15} and H^{14}, respectively (see Electronic Supplementary Information, ESI). Thanks to its low solubility, *meso*-**1** easily crystallized in the centrosymmetric $Ccm2_1$ space group, with the nitrogen atoms of adjacent pyridyl rings disposed *trans* to one another, as is usual in 2,2':6',2"-terpyridines (Scheme 2a).[8] The structure also confirms (*i*) the C_s symmetry of the achiral *meso* compound; (*ii*) the high degree of planarity of the

terpy moiety (dihedral angles between the different pyridine rings < 6.5°); and (*iii*) values for the helical angle (angle between the terminal rings) of the azahelicene moieties that are typical of such units (51.83°).[3]



Scheme 2. a) Coordination of achiral ligand *meso*-**1** to Zn^{2+}, generating *meso*-**1**·$Zn(OAc)_2$ and their respective X-ray crystal structures. b) X-ray structure and supramolecular arrangement of (*P*,*P*)-**1** along the *x* axis in the solid state.

Pure samples of (*M*,*M*)- and (*P*,*P*)-**1** were successfully obtained from the crude stereoisomeric mixture by using HPLC over a chiral stationary phase and were then fully characterized (see ESI). They display different ^{1}H NMR spectra from the *meso*-**1** compound in agreement with different orientation of helicenic moieties (for instance H^{15} and H^{14} resonate at 6.7 and 7.1, ppm, respectively). The X-ray structure of (*P*,*P*)-**1** ($P2_122_1$ space group; Scheme 2b) shows (*i*) C_2 symmetry as opposed to the C_s symmetry of the *meso* isomer; (*ii*) again a high degree of planarity within the terpy moiety (dihedral angles between the pyridine rings < 8.3°) and a *trans* disposition of N atoms in adjacent rings; and (*iii*) typical values for the helical angle of the azahelicene moieties (60.84°).[3] Furthermore, compound (*P*,*P*)-**1** displays intermolecular organization along the *x* axis thanks to the presence of π–π interactions (centroid-centroid distances 3.67 Å; Scheme 2a).

Compounds *meso*-**1** and (*P**,*P**)-**1**[#] display photophysical properties with similar characteristics to one another (see ESI). For example, the UV-visible spectra of these two compounds show a very strong absorption band centred at about 320 nm ($\varepsilon \sim 6 \times 10^4$ M^{-1} cm^{-1}) and a set of bands extending into the visible region, of gradually diminishing intensity, of which the longest wavelength appears at 416 nm ($\varepsilon = 5 - 8 \times 10^3$ M^{-1} cm^{-1}). (*P**,*P**)-**1**[#] displays intense blue fluorescence in CH_2Cl_2 at r.t. (λ_{max} = 421 nm, ϕ = 8.4%, τ = 5.7 ns). Its structured emission spectrum is characterised by a vibronic progression of ~ 1350 cm^{-1}, with the maximum intensity being in the 0-0 band, indicative of a rigid aromatic fluorophore. In a frozen glass at 77 K, the fluorescence is accompanied by long-lived green phosphorescence (λ_{max} = 532 nm, τ = 1.4 s), with similar vibrational structure. Similar spectra were recorded for *meso*-**1**. The emission properties are in line with previously described nitrogen-containing [6]helicene derivatives.[5d]

The chiroptical properties of (*M*,*M*)- and (*P*,*P*)-**1** were then studied. High specific and molar optical rotation values were obtained ((*P*,*P*)-**1**: $[\alpha]_D^{23}$ = +2150, $[\phi]_D^{23}$ = +15790 (±5%, CH_2Cl_2, 2.2 × 10^{-4} M). The molar rotations are twice as high as for 4-aza[6]helicene ($[\alpha]_D^{23}$ = +2290, $[\phi]_D^{23}$ = +7735 ° cm^2/dmol (± 5%, CH_2Cl_2, *C* 1.7 g/100mL))[9] in agreement with the presence of two azahelicene moieties. Similarly, very strong mirror-image ECD spectra were recorded for (*M*,*M*)- and (*P*,*P*)-**1** enantiomers (Figure 1), with a strong negative band around 264 nm ($\Delta\varepsilon$ = -280 M^{-1} cm^{-1}) and strong positive one at 341 (+388 M^{-1} cm^{-1}) for the (*P*,*P*)-**1** enantiomer. Interestingly, a clear substructure is appearing and is assigned to a vibronic progression (~ 1350 cm^{-1}, C=C stretching bands). A weak positive ECD band ($\Delta\varepsilon$ = +21 M^{-1} cm^{-1}) is also present at 420 nm.

CPL activity is another appealing chiroptical property of organic chiral chromophores such as helicenic derivatives and has been examined recently by us and others.[10] Indeed (*M*,*M*)- and (*P*,*P*)-**1** enantiomers demonstrated mirror-imaged CPL spectra (Figure S20) with opposite g_{lum} values ((*P*,*P*)-**1**: +8.6 × 10^{-3} and (*M*,*M*)-**1**: -8.4 × 10^{-3}) around the emission maximum (~ 420 nm). These values are slightly stronger than for related molecules such as helicene-bipyridine derivatives (g_{lum} ~ ±10^{-3})[5d] or other CPL-active organic molecule.[11]

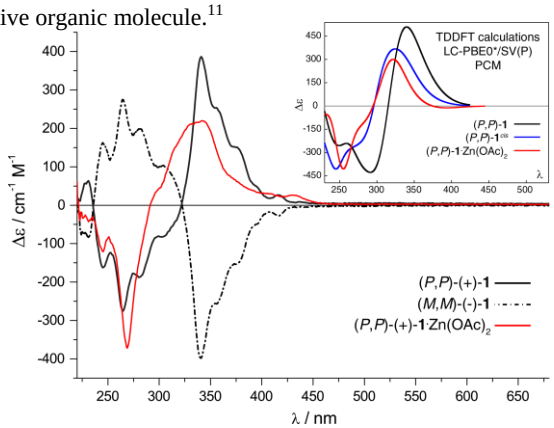


Figure 1. Experimental ECD spectra of enantiopure (*M*,*M*)- and (*P*,*P*)-**1** and its Zn(II) complex (*P*,*P*)-**1**·$Zn(OAc)_2$ (CH_2Cl_2, 2 × 10^{-5} M). Inset: Simulated spectra of (*P*,*P*)-**1** (*trans* and *cis*) and (*P*,*P*)-**1**·$Zn(OAc)_2$ (see ESI).

The terpyridine system is a good scaffold for coordination to a variety of transition-metal centers yielding complexes with a rich variety of photophysical properties that may be appealing for device applications.[8,12] Rarely have chiral substituents been integrated within the terpy scaffold and used as chiroptical switches or chiral sensors.[13] In 2004, Lehn *et al.* described a two-state switching system based on a terpyridine-type receptor which was activated towards substrate binding upon complexation of a zinc(II) cation.[12a] This process was based on so-called "nanomechanical motions" induced by ion binding and involving shape switching between two forms presenting different physicochemical properties, namely the metal-bound and the metal-free states. Inspired by this seminal work, we explored how Zn(II) binding to **1** could induce chemical switching of the (chir)optical properties through the large conformational changes associated with the switch from W- to U-shape geometries of the terpy moiety (Figure 2b).

In the first instance, *meso*-**1**·$Zn(OAc)_2$ complex was prepared

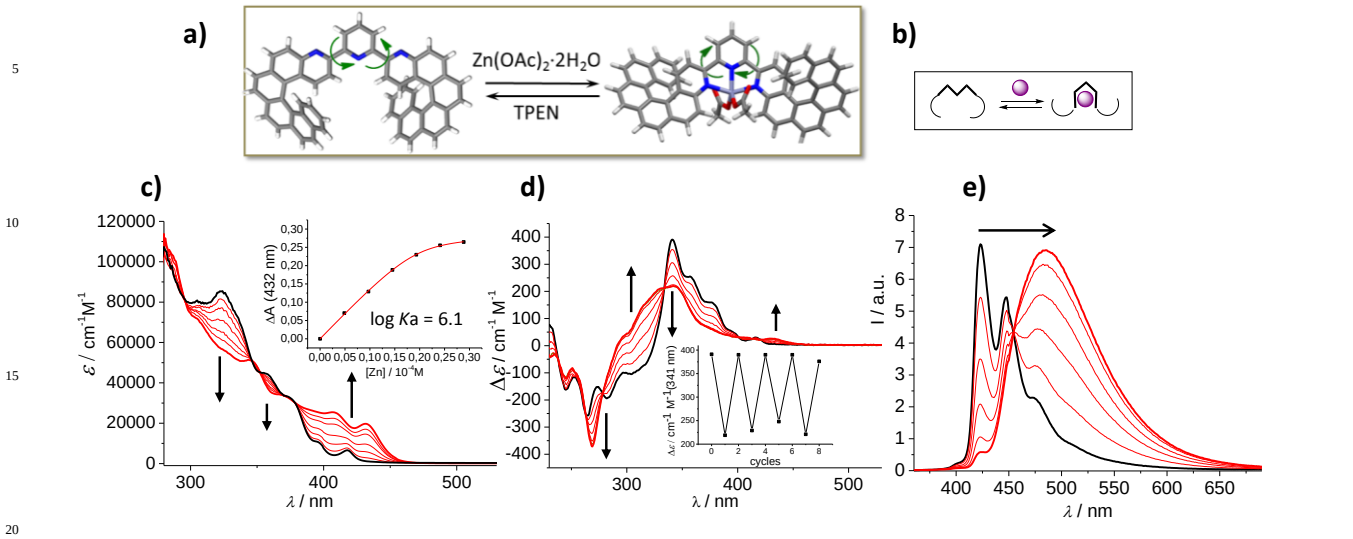


Figure 2. a) Reversible Zn(II) complexation-decomplexation process of (*P*,*P*)-**1** using $Zn(OAc)_2$ and TPEN as the chemical stimuli. b) Schematic modification of the geometry. c) Evolution of the UV-vis spectrum of (*P**,*P**)-**1**$^{\#}$ (3×10^{-5} M, CH_2Cl_2, rt) upon addition of $Zn(OAc)_2{\cdot}2H_2O$ aliquots (0.2 equiv. until saturation at 1.0-1.2 equiv.). Inset: Absorption at 432 nm and fitting with a 1:1 binding model. d) Evolution of the ECD spectrum of (*P*,*P*)-**1**. Inset: Reversible ECD_{341nm} switching process. e) Evolution of the fluorescence of (*P*,*P*)-**1** (λ_{ex} = 350 nm, 2.2×10^{-5} M, CH_2Cl_2, r.t.).

from *meso*-**1** ligand upon treatment with 1 equiv. of I $Zn(OAc)_2{\cdot}2H_2O$ in CH_2Cl_2 (see Scheme 2). This complex was obtained quantitatively (K_a = 1.98 × 10^6 M^{-1}) and was fully characterized (see ESI). Single crystals could be grown and the X-ray structure ($P12_1/n1$ space group, Scheme 2a) shows the pentacoordinated Zn centre, with two OAc and the terpy ligand in a *cis* geometry (U shape). Note that upon coordination, the *meso*-**1** ligand has kept its C_s symmetry but the helical angle of the aza[6]helicene parts has increased to 77.72°, certainly due to steric hindrance. Overall, upon coordination to the metal ion, the two aza[6]helicene moieties have fully rotated around the C–C bonds from one side of the central pyridyl ring to the other, thus inducing significant conformational change.

In a second stage, aliquots of $Zn(OAc)_2{\cdot}2H_2O$ were added to (*M*,*M*)- and (*P*,*P*)-**1** and the complexation process (Figure 2a,b) was followed by UV-vis and ECD spectroscopy (0.2 equivalents of $Zn(OAc)_2$ were added until saturation at 1.0-1.2 equiv.). Large changes were observed in the UV-vis spectrum of (*P**,*P**)-**1**$^{\#}$ upon Zn(II) binding, as depicted in Figure 2c, with the presence of several isosbestic points, showing that the two species are in equilibrium. The solution turned from pale yellow to dark yellow colour. Curve fitting of the absorption variation at 432 nm revealed the formation of a 1:1 binding model with a high association constant (K_a = 1.16 × 10^6 M^{-1}). Substantial modifications were also observed for chiroptical properties of (*P*,*P*)-**1** upon Zn(II) binding (see Figure 1 and 2d). For example, the strong, positive ECD-active band at 341 nm decreases from +388 to +220 M^{-1} cm^{-1}, a band around 310 nm increases and gains significant positive intensity (from -70 to +90 M^{-1} cm^{-1}), and a new positive band of low intensity appears at 430 nm ($\Delta\varepsilon$ = +26 M^{-1} cm^{-1}), while the molar rotation slightly increases ((*P*,*P*)-**1**·$Zn(OAc)_2$: $[\alpha]_D^{23}$ = +2300, $[\phi]_D^{23}$ = +17300 (±5%, CH_2Cl_2, 2.18 × 10^{-4} M), *vide supra*). Similarly, the luminescence profile of **1** significantly changes upon adding $Zn(OAc)_2$, with the appearance of a structureless intense fluorescence emission at 480 nm (ϕ = 19%, τ = 3.4 ns, see Figure 2e) and CPL activity at this wavelength with g_{lum} values of +1.2 × 10^{-3} and -1.4 × 10^{-3} for (*P*,*P*)-**1**·$Zn(OAc)_2$ and (*M*,*M*)-**1**·$Zn(OAc)_2$, respectively (see ESI). The emission colour turned from blue to green.

Calculations at the LC-PBE0*/SV(P) level[14] with a continuum solvent model for CH_2Cl_2 reproduce these modifications well and link them predominantly to the large conformational changes in the structure of the ligand **1** upon Zn(II) coordination. The simulated ECD spectrum of ligand **1** in the *cis* conformation of the terpy unit indeed clearly resembles the one calculated for **1**·$Zn(OAc)_2$ (Figure 1). Additionally, the Zn(II) complexation has a strong effect on the LUMO and LUMO+1 of **1** (both π*), leading to a concentration of their density around the zinc ion in the terpyridine part of the ligand (see SI for the MO analysis).[5d] The HOMO and other high lying occupied π-orbitals remain helicene-centered and therefore the complexation strongly increases the character of charge-transfer from the helicene to the terpyridine part of the ligand in the low-energy part of the spectrum.[5d] Note that no Zn orbitals were found to contribute to the π-conjugated system of the helicene ligand, as expected for closed-shell d^{10} metal centers. The primary effect of the Zn moiety is therefore to activate the structural transformation of the aza[6]helicene fragments, rigidify the system, and induce charge-transfer excitations within the ligand. The calculations also correctly reproduce changes in the S_1-S_0 (HOMO-LUMO) emission upon Zn(II) complexation, which is in line with the noticeable energetic stabilization of the LUMO in the complex relative to the pristine ligand: from 419 nm, g_{lum} = + 6.8 × 10^{-3} computed for (*P*,*P*)-**1** to 452 nm, g_{lum} = + 1.1 × 10^{-3} for (*P*,*P*)-**1**·$Zn(OAc)_2$ (*vide supra*, see ESI).

In order to verify the reversibility of the Zn(II) binding process, *N*,*N*,*N*',*N*'-tetrakis(2-pyridylmethyl)ethane-1,2-diamine (TPEN) was utilized as a competitive ligand for zinc: upon treatment with TPEN, the system returned to its original state, *i.e.*

to the native chiral (*P*,*P*) and (*M*,*M*)-**1** ligands. Up to 9-10 steps could be performed upon successive additions of 1 equiv. of $Zn(OAc)_2$ and TPEN, following the ECD tuning at a selected wavelength where the changes are very high (for example $\Delta\Delta\varepsilon$ = 175 M^{-1} cm^{-1} at 341 nm, see inset of Figure 2d). Overall, this system is behaving as a chiroptical switch offering multi-output read-out (UV-vis, ECD, luminescence and CPL). Furthermore, the switching process triggers conformational changes and molecular motion around the Zn centre, from a clear *trans* (W-shape) conformation in the free ligand to a *cis* (U-shape) one in the Zn-complex. To our knowledge, this constitutes a new type of helicene-based chiroptical switching.[4] In conclusion, the preparation of unprecedented bis-helicenic terpy ligand has opened new perspectives in multifunctional chiral complexes and chiroptical switches; coordination to other metallic ions is under current investigation.

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Notes and references

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† Electronic Supplementary Information (ESI) available: synthetic, spectroscopic and computational details. See DOI: 10.1039/b000000x/

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