Recent results on some columnar paramagnetic metallomesogens

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Abstract. The liquid crystalline and selected physical properties of some vanadyl and manganese(III)-porphyrin-TCNE complexes are discussed. These materials form linear chains from a magnetic point of view and columnar discotic LC phases. Some of the manganese complexes exhibit a bulk magnetic phase below $\sim$20 K. The discussed materials are studied by means of DSC, X-ray powder diffraction, dielectric spectroscopy, reversal current characterization and magnetic susceptibility measurements. A broader view on some physical properties of columnar paramagnetic metallomesogens is given.

1. Introduction

Discotic liquid crystals or columnar mesophases have been known since their discovery by Chandrasekhar *et al* [1] who found that flat organic molecules assembling disc-like entities exhibit intermediate phases between the solid and the liquid state. Because these liquid crystals form 1d-ordered or disordered stacks in a two-dimensional array, there are expectations for charge carriers mobility or electronic transport properties along the stacks, good for application e.g. in molecular scale FETs, in p–n junctions, in light sensors due to photoluminescence properties, etc. So far, strong R&D activities go in that direction.

If a metal ion is incorporated within the flat organic molecule or situated in between like in rare earth phthalocyanines, some additional properties characterizing the metal ions in their environment arises: the electronic properties which can introduce or accumulate the electro- or photo-luminescence and magnetic properties in case of open shell systems leading to one-dimensional magnetic complexes and sometimes bulk magnetic, catalytic and sensor properties.

The increase of electrical conductivity up to the order of semiconductors was reported in [2–4] and the appearance of strong photoluminescence and photoconductivity was reported in [5].

In this paper we will focus on two kinds of materials we recently dealt with. One is the class of some vanadyl complexes by Swager *et al* [6,7] recently investigated by us [2–4]. The molecular structure of one of the compounds is described in figure 1. In the solid state and in the highly ordered LC state there are –V=O–V=O– alternating chains, characterized by IR spectra, X-ray diffraction, magnetic measurements, electro-optical studies and dielectric investigations.

The second class of compounds is from the Mn(III)-porphyrin-TCNE family (TCNE=tetracyanoethylene). In these, the discotic behaviour was evident at higher temperatures, having very interesting but different magnetic behaviour in the low temperature state (∼20 K), depending on the porphyrin system used.

The principal structure is presented in figure 2. The synthesis and the characterization was described in [8]. With this kind of material we will address the question if the LC state is a precursor for specific arrangements in the solid state.
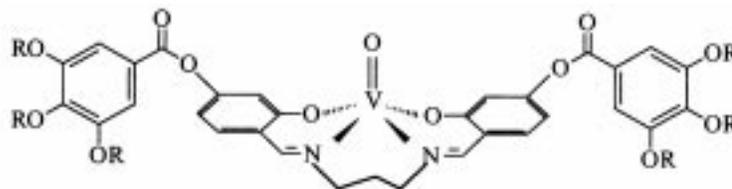

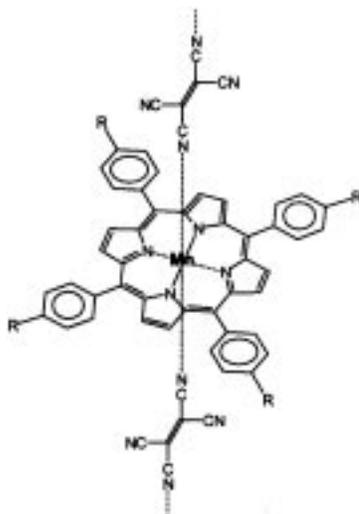**Figure 1.** Molecular structure of a selected VO-compound, *R*=alkyl group.

Figure 2. Chemical structure of the Mn(III)-TP′P-TCNE complexes, *R*=alkyl or alkoxy group.

2. Vanadyl complexes

2.1 *General*

The chemical structure of one of the investigated molecules is displayed in figure 1. As was evident by X-ray crystal structure determination in the solid state on a homologous compound [6,7] there is a –V=O–V=O– linear chain with V···V distances by 3.84 Å, V=O 1.63 Å and V–O 2.21 Å. In the liquid crystalline state, the molecules favour dimeric building blocks so that two neighbouring molecules in the columnar mesophases form disc-like entities which split in the isotropic phase into monomers. The phase transition temperatures were observed by DSC for three compounds of that series, and is presented in table 1 [2–4].

There are at least two crystalline phases, one called ODIC-phase (orientationally disordered phase) and three discotic phases Col_{ro}, Col_{rd}, Col_{hd}, characterized by DSC, polarizing microscopy and X-ray diffraction.

Because of the dipolar structure of the molecules on one side and the paramagnetism of the V(IV)-center ($3d^1$-system) some interesting linear dielectric and magnetic properties are to be expected.

2.2 *Temperature dependence of the conductivity and the dielectric relaxation processes*

The experimental technique used is described in [2–4]. The frequency domain dielectric spectroscopy has been applied in the frequency range 10 mHz–13 MHz, covering at all 9 decades.

The temperature dependence [2–4] of the conductivity in (S/m) start from 10^{-9} for the crystalline phase at room temperature and is increased by raising the temperature up to 10^{-5} S/m (from insulators to semiconductors) as is discussed several times in the literature for discotic systems. In our understanding, this conductivity is not of an electronic origin but due to ions with increased mobility by decreasing the temperature.

The dielectric spectrum is hard to interpret (see figure 3). The different relaxation processes observed are described in detail in [2–4]. In all the discotic Col_{ro} phase the lower frequency process C is assigned as a diffusional reorientation of the columnar polar chains. At higher temperatures in the Col_{hd} phase and the isotropic phase the process B exists and

Table 1. Phase transition temperatures of vanadyl complexes.

Compound	R	Phase transition temperature (°C)
1(10)	$C_{10}H_{21}$	Cr_1 85 Cr_x 119 Col_{ro} 153 Col_{rd} 172 Col_{hd} 180 I
1(12)	$C_{12}H_{25}$	Cr_1 48 Cr_2 68 Cr_x 100 Col_{ro} 141 Col_{rd} 157 Col_{hd} 182 I
1(14)	$C_{14}H_{29}$	Cr_1 68 Cr_2 82 Cr_x 93 Col_{ro} 140 Col_{hd} 188 I

Cr_1 and Cr_2: crystalline phases; Cr_x: ODIC-phase (orientationally disordered crystalline phase); Col_{ro}: rectangular ordered columnar discotic phase; Col_{rd}: rectangular disordered columnar discotic phase; Col_{hd}: hexagonal disordered columnar discotic phase; I: isotropic phase.
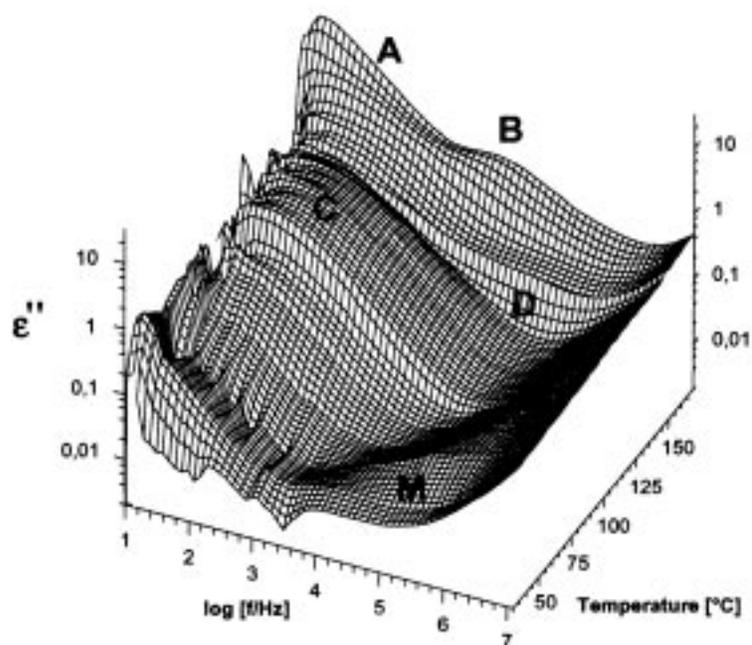
Figure 3. Dielectric relaxation processes in different columnar phases of vanadyl compound 1(12) (from [2]).

it is assigned as diffusional reorientation around the long molecular axis. The process D in the Col_{rd} phase is assigned as rotational relaxation of the molecules inside the column.

Interestingly at lower temperatures, within the orientationally disordered phase the process M appears, which is in some way comparable to the β-process showing WLF behaviour in glass forming materials. At higher temperatures and low frequencies (see figure 3) a very intense process A exists, which is not of molecular origin but due to some ions leading to interfacial polarization as described for other LC materials before [9].

2.3 *Magnetic properties*

The experimental technique and the principal results for several investigated compounds are presented in [4]. If there are some coupling effects between the paramagnetic centers, then one can control by measuring the magnetic susceptibility χ down to lower temperatures. If the product of the susceptibility and temperature χT (or the effective magnetic moment μ_{eff} in units of the Bohr magneton μ_B) is constant over the broader temperature region, no coupling effects exist (neglecting special effects). In our case [4] (see figure 4) the magnetic moment at lower temperature increases, indicating a ferromagnetic coupling, e.g. spins at the centers are parallely aligned. Because the calculated coupling constant $J = 4.6\,\mathrm{cm}^{-1}$ (using a Hamiltonian $\hat{H} = -2J\sum_{i=1}^{a} S_i J S_{i+1}$) for a linear chain (Landé factor $g = 2.04$, amount of uncoupled VO^+ centers = 2.7%) is rather weak but no change in the phase transitions is visible, one can expect ferromagnetic exchange interaction even in the discotic phase.
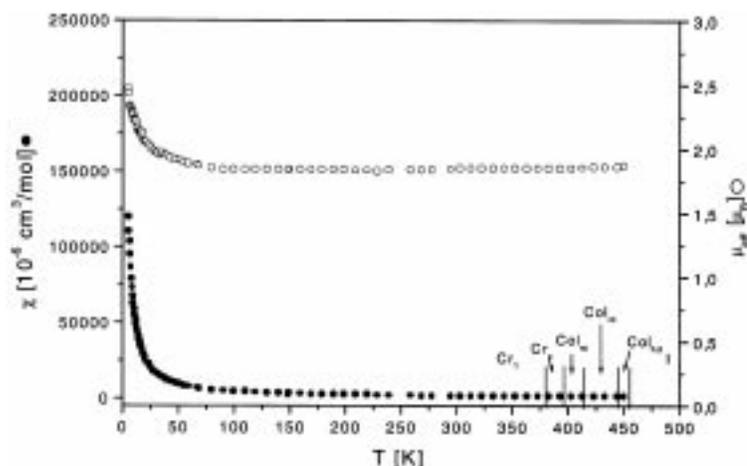
Figure 4. Magnetic behaviour of the VO-complex 1(10) (from [4]).

2.4 *Polarization reversal current measurements and switching experiments*

To our surprise one could detect [2–4], by measurements with a triangular wave within the Col$_{ro}$ phase, reversal current peaks and from that one could calculate a hysteresis loop. The point is, the so-calculated spontaneous polarization does not show the typical temperature dependence and is visible only at low frequency. Surprisingly such reversal current peak could even be seen in the nematic and isotropic phases of some salicylaldimine compounds, so we do not think that there is a need to interpret the behaviour as ferroelectricity.

Switching was not visible under a polarizing microscope. But we have to be careful because the optical axis does not change by homeotropic orientation.

3. Mn(III)-porphyrin-TCNE complexes

3.1 *General*

The liquid crystalline behaviour of some porphyrin derivatives is well-documented [10,11] including the LC properties of some metalloporphyrins. This kind of compound is a very good example of a transition from calamitic to discotic systems depending on the number of substituents phen-*R* (for the series with *R* being a substituent on the phenyl system, e.g. $R = OC_{12}H_{25}$) having Zn centers [12].

The metal-free *para*-alkylphenyl substituted porphyrins were described as forming lamellar phases [13]. The corresponding *para*-alkoxyphenyl compounds do not show LC phases at all but at least some exhibit different crystalline phases.

Our interest originates from the magnetic aspects and we synthesized several Mn(III)-TP′P-TCNE complexes (TP′P=substituted tetraphenylporphyrin, TCNE=tetracyanoethylene). The synthesis is described elsewhere [8]. Because of some aspects in explaining the very interesting magnetic properties some analytical control along the synthetic route
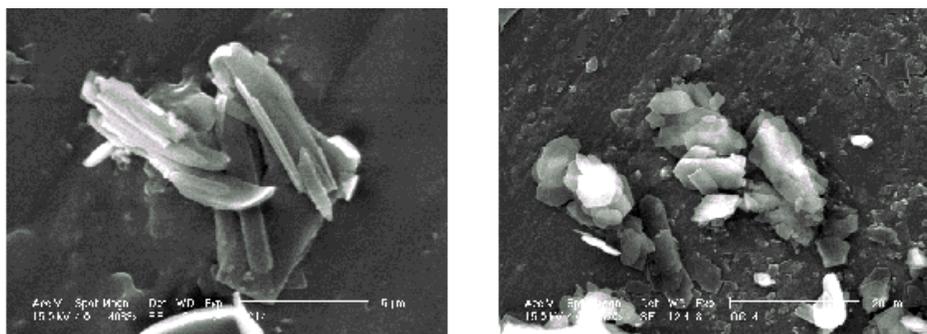
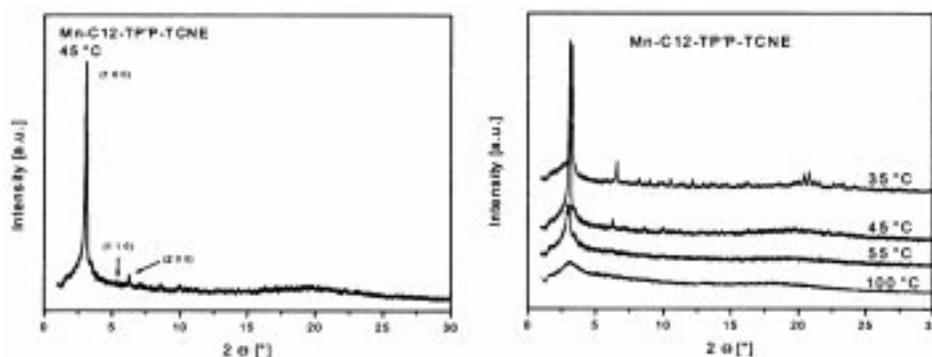**Figure 5.** REM investigation of Mn-OC14-TP′P-TCNE.

Figure 6. X-ray investigation of Mn-C12-TP′P-TCNE.

by REM microscopy was fulfilled (figure 5). One can see that no paramagnetic nanoscale impurities are incorporated.

3.2 *DSC and X-ray investigation*

The DSC investigations were done on a commercial Perkin–Elmer DSC 2C. The equipment used for X-ray powder diffraction was a STOE Stadi 2 diffractometer with a position-sensitive detector STOE mini PSD.

In agreement with Shimizu *et al* [13], C10-TPP exhibits one and C12-TPP exhibits two LC phases between the crystalline and the isotropic phases.

The Mn(III)-TP′P-TCNE with C12-substituent shows LC behaviour, indicated by DSC and X-ray diffraction pattern assigned by us as Col_{hd} phase with the reflections (100) at $2\Theta = 3.1°$ (very weak), (110) at $2\Theta = 5.4°$ and (200) at $2\Theta = 6.3°$ and a broad, diffuse peak in the wide angle area indicating a hexagonal disordered phase (see figure 6). In the DSC run only the transition to the LC phase could be detected and not the clearing point, perhaps due to reduced thermal stability of the complex at higher temperatures.

The alkoxy-substituted compounds behave differently. Mn-OC12-TP′P-TCNE (with a dodecyloxy tail on the phenyl rings) was described to exhibit a Col_{ho} phase with Cr 108°C
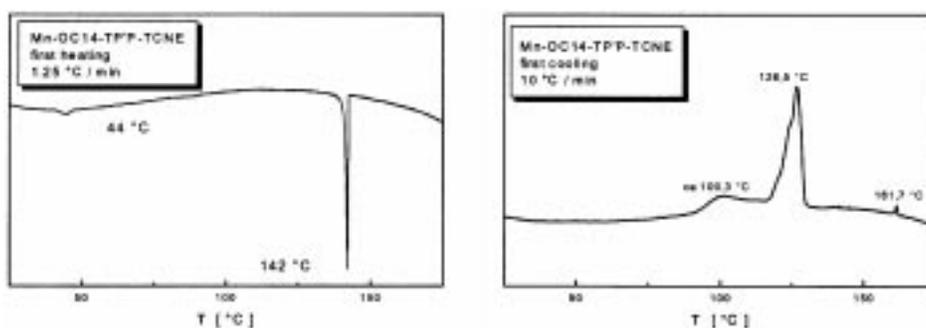
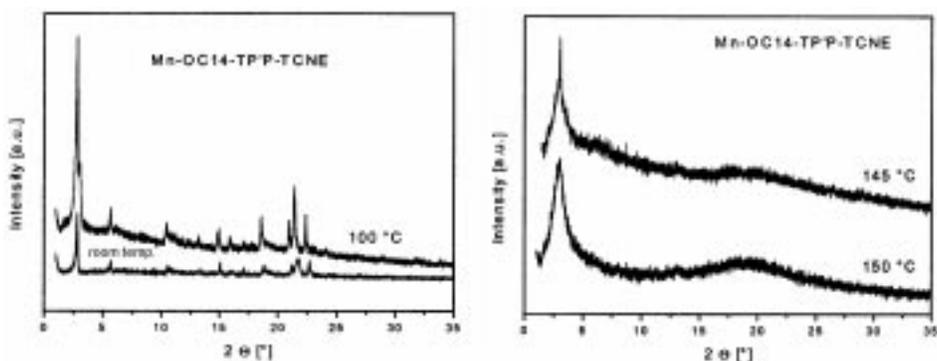**Figure 7.** DSC investigation of Mn-OC14-TP′P-TCNE.

Figure 8. X-ray investigation of Mn-OC14-TP′P-TCNE.

(20.6 kJ/mol) Col_{ho} 155°C (10 kJ/mol) I [14]. Similar behaviour could be found for Mn-OC10-TP′P-TCNE. In contrast to the lower homologues with OC10 or OC12 groups Mn-OC14-TP′P-TCNE exhibits a disordered phase as indicated by a diffuse peak in the wide angle area. The DSC data for Mn-OC14-TP′P-TCNE are shown in figure 7 with a phase sequence C_1 44°C C_2 142°C Col_{hd} ~170°C I.

In figure 8 the X-ray pattern for RT, 100°C, 145°C and 150°C are presented. There is a strong small angle reflection in the Col_{hd} phase and a broad wide angle reflection due to chain melting and weak reflections ((110), (200)).

We cannot explain at the moment why the higher homologue (OC14) forms a disordered phase, and the lower homologues (OC10, OC12), ordered phases.

3.3 *Magnetic behaviour*

The static magnetic susceptibilities were measured on a Faraday magnetometer built with a CAHN D200 microbalance, a Bruker magnet system B-E 20, and a Leybold-Heraeus cryostat. A detailed description can be found elsewhere [15].

In figure 9, the magnetic susceptibility χ and the effective magnetic moment μ_{eff} of one alkyl (Mn-C12-TP$'$P-TCNE) and one alkoxy (Mn-OC14-TP$'$P-TCNE) complex are plotted to show the difference in the low temperature magnetic behaviour.

The alkyl compounds do not contain a magnetically ordered phase. Pure Curie–Weiss properties are observed in the temperature range from 4.5 to 300 K with a decrease of $\mu_{\text{eff}}(T)$ down to low temperatures due to zero-field splitting of the Mn(III) ions. The magnetic properties can be fitted well with a Weiss constant $\Theta = -5$ K.

In contrast to this, the alkoxy-substituted compounds show a dramatic increase and a maximum of $\mu_{\text{eff}}(T)$ at low temperatures far above the value of a ferromagnetically coupled dimer of Mn(III) ions and an organic radical. The behaviour can be fitted by assuming a linear chain of alternating Mn(III) ions and organic radicals with an exchange coupling of $J = -102.8$ cm^{-1} according to Drillons law [16] with a Hamiltonian of the type $\hat{H} = -J\sum_{i=1}^{2N} S_i J S_{i+1}$. At $\sim$20 K the compounds show a phase transition to a bulk magnetic phase [17]. The transition temperature to this phase depends on the applied pressure [18]. The necessary three-dimensional coupling is caused by a dipolar interaction between neighbouring chains [19]. The transition temperature from the paramagnetic to the bulk magnetic phase can be investigated by means of dynamic magnetic susceptibility. The properties of the bulk magnetic phase can be investigated by magnetization measurements (e.g. hysteresis) [20]. At higher temperatures these linear ferrimagnetic chains show a minimum in a plot of $\mu_{\text{eff}}(T)$. The stronger the coupling between the spin carriers the higher is the temperature of the minimum. The fact that this minimum is not observed up to 300 K indicates that the magnetic coupling is still present in this temperature region. So one could still characterize this compound as a linear chain from the point of view of magnetic behaviour in the LC phase.

The question arises, why is there such a big difference in the magnetic behaviour of the alkyl and the alkoxy compounds at low temperatures? The different properties can be understood when taking into account the structural differences. The phase transition to the LC phase in the alkyl compounds is at lower temperatures (30–100°C) than in the alkoxy homologues and it is a disordered phase. Even though Mn-OC14-TP$'$P-TCNE exhibits a disordered phase, the transition is at higher temperatures. It seems that the LC properties at lower temperatures hinder the structural pre-packing favourable for the bulk ferromagnetism. Most probably the disordered phase at lower temperatures prevents the building up of large linear chains as there are no hints of linear chain magnetic behaviour observed in the magnetic measurements of the alkyl compounds. It was recently shown
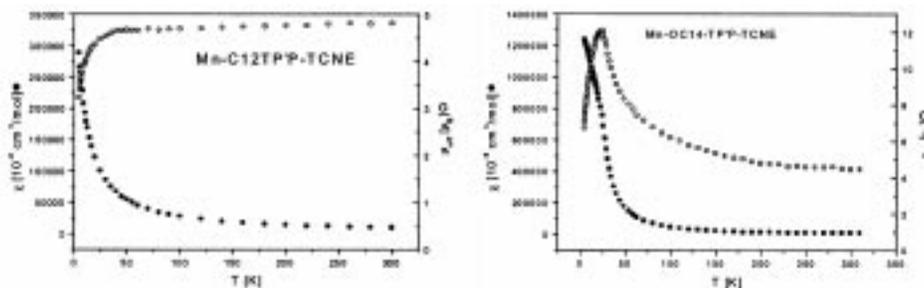

Figure 9. $\chi(T)$ and $\mu_{\text{eff}}(T)$ for the alkyl-substituted Mn-C12-TP$'$P-TCNE (left) and the alkoxy-substituted Mn-OC14-TP$'$P-TCNE (right).

that the alkyl-substituted compounds can also exhibit a ferrimagnetic linear chain structure and probably a bulk magnetic phase when the bridging ligand is changed from TCNE to TCNQ (TCNQ=tetracyanoquinodimethane) [21].

4. Discussion

The results presented show some physical effects, one typical for a discotic liquid crystal and the other characterizing paramagnets. Some of the effects presented are combinations of the discotic LC properties and the paramagnetic centers. We discussed for the vanadyl compounds the enhanced conductivity which most probably is along the one-dimensional chain due to ions. The magnetic properties of both classes of materials demonstrated a one-dimensional ferromagnetic chain for the vanadyl complexes and a ferrimagnetic chain for the Mn-TP$'$P-TCNE compounds resulting due to the antiferromagnetic coupling of Mn(III) ions ($S = 2$) and TCNE radicals ($s = 1/2$). But as discussed, the alkyl-substituted compounds do not show the properties of a magnetic linear chain.

Since many supporting experiments like X-ray and detailed dielectric measurements for the vanadyl complexes were done, we are confident that in the highly ordered phases of this compound, some restricted ferromagetically coupled chains or at least oligomers are present. One can speculate that –Mn–TCNE–Mn oligomers might be present in the LC state of the alkoxy-substituted compounds too. Furthermore, the understanding of the existence of three-dimensional ferromagnetism at low temperatures assuming only an exchange interaction model is not clear, and hence dipolar coupling effects are most probably responsible for this bulk magnetic phase, based on the anisotropy of the Mn(III) ion [19].

Unfortunately the anisotropy of the alignment of the LC state could not be studied in the presented compounds but strong magnetic anisotropy is a well-known phenomena particularly in rare earth metallomesogens [22,23]. Here, the macroscopic anisotropy of the LC state strongly depends on the anisotropy of the central metal ion.

For example, for some Dy(III) complexes aligned perpendicular to the external magnetic field [22] anisotropic data of $\Delta\chi \sim 20 * 10^{-3}$ cm^3/mol or even up to $-40 * 10^{-3}$ cm^3/mol [24], whereas some Er(III) complexes align with $\Delta\chi \sim +1.6 * 10^{-3}$ cm^3/mol parallel to the field.

Another interesting feature of paramagnetic metallomesogens are their optical properties. Strong dichroism can be measured by absorption experiments and by luminescence or photoluminescence [5,22,23].

All these described properties demonstrate the usefulness of materials based on calamitic and discotic metallomesogens.

Acknowledgement

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