

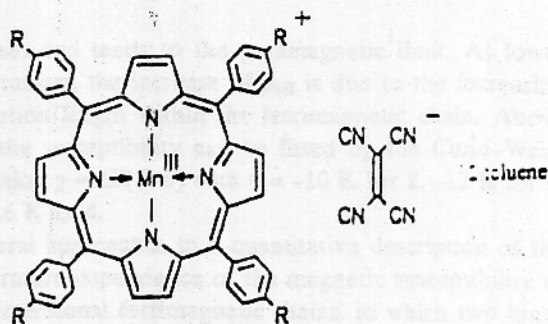
# A Ferrimagnetically Coupled Liquid Crystal\*\*

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Metallomesogens are very attractive candidates for novel advanced materials,<sup>[1,2]</sup> and a great deal of current research is devoted to metallomesogens on account of their magnetic properties.<sup>[3-7]</sup> The structural order in a mesogenic phase may enable the existence of magnetically ordered structures, however, materials which combine mesogenic with ferro- or ferrimagnetic exchange coupling or bulk properties such as ferro- or ferrimagnetism have not been reported.

In 1978, Summerville et al. reported the unusual magnetic properties of the complex  $[Mn^{III}(TPP)](TCNE) \cdot 2$  toluene (1) (see Figure 1; R = H; TPP = tetraphenylporphyrin; TCNE = tetracyanoethylene).<sup>[8]</sup> In 1992, a detailed characterization of this compound, including X-ray structure determination, magnetization, magnetic hysteresis, and temperature-dependent magnetic susceptibility measurements, was reported by Miller et al.<sup>[9]</sup> The structure determination identified an alternating chain structure with  $TCNE^{\ominus}$  bridging two manganese(III) ions through nitrogen atoms in the *trans*-position and the presence of two toluene solvent molecules per chain unit.

The possibility of combining the bulk magnetic properties of ferrimagnetic chains as observed for 1 with the liquid-crystalline behavior of metal-containing mesoporphyrins<sup>[10,11]</sup> prompted us to prepare and examine the dodecyloxy-substituted compound  $Mn^{III}[(OC_{12}H_{25})_4TPP](TCNE) \cdot 2$  toluene (2) (see Figure 1; R =  $OC_{12}H_{25}$ ). In this paper, we present the results of our static and AC susceptibility measurements on this complex, which combines liquid-crystalline properties above 381 K with ferrimagnetic properties below 21.4 K. The liquid-crystalline properties were investigated by means of differential scanning calorimetry (DSC) and X-ray investigations. Additionally, AC susceptibility investigations on the homologous methyl- and methoxy-substituted compounds  $[Mn^{III}((CH_3)_4TPP)](TCNE) \cdot 2$  toluene (3) and  $[Mn^{III}((OCH_3)_4TPP)](TCNE) \cdot 2$  toluene (4) were performed in order to establish the onset



- R = H (1)  
R =  $OC_{12}H_{25}$  (2)  
R =  $CH_3$  (3)  
R =  $OCH_3$  (4)

Fig. 1. Chemical structure of the investigated compounds 2, 3, 4 and of the complex 1 described by Summerville et al. [8] and Miller et al. [9].

of a three-dimensional (3D) magnetic ordering at low temperatures in these compounds. The synthesis and static magnetic susceptibilities of the non-mesogenic compounds 3 and 4 have been reported recently.<sup>[12,13]</sup>

The thermodynamic data of complex 2 are  $C_{108}^{\circ}C$  (20.6 kJ/mol)  $D_{ho}$  155 $^{\circ}C$  (10.1 kJ/mol) i. e., the complex exhibits a discotic mesophase in the temperature-range 108–155 $^{\circ}C$ . The mesophase of complex 2 was characterized by X-ray powder diffraction at several temperatures. The X-ray diffraction pattern of complex 2 at 123 $^{\circ}C$  is given in Figure 2. The strong low angle peak is characteristic of a hexagonal columnar lattice and is hence assigned as the 100 reflection, corresponding to an intercolumnar distance of 30.8 Å. This spacing is in very good agreement with the expected length of the molecular "side" (from the end of one alkyl-chain to the end of an adjacent alkyl chain as reported in the literature.<sup>[15]</sup> The other low angle peak at 13.7 Å is approximately where the 200 reflection of a hex-

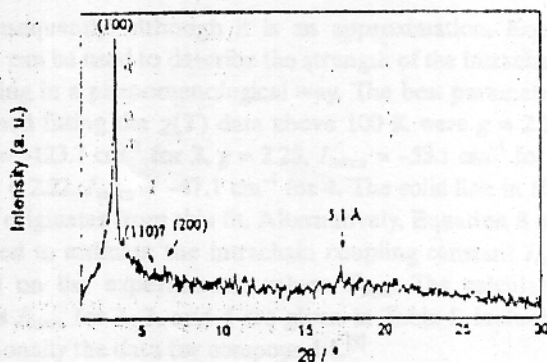


Fig. 2. X-ray diffraction from the  $D_{ho}$  phase at 123 $^{\circ}C$  of complex 2.

agonal lattice is expected. The 110 reflection has a very weak intensity. There is a weak wide angle peak at 5.1 Å. This spacing most probably corresponds to the distance be-

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tween porphyrin and the center of TCNE<sup>⊖</sup>, which is similar in crystalline Mn<sup>III</sup>-porphyrin/TCNE complexes (= 5 Å).<sup>[10]</sup> It can be concluded from these results that complex 2 shows a discotic hexagonal ordered columnar (D<sub>ho</sub>) mesophase.

The temperature dependence of the effective magnetic moments  $\mu_{\text{eff}}$  for compound 2 is presented in Figure 3. The data for 3 and 4 are consistent with those already reported in the literature.<sup>[12,13]</sup> All compounds exhibit essentially the same temperature dependence of the effective magnetic moments  $\mu_{\text{eff}}$  as reported for [Mn<sup>III</sup>(TPP)](TCNE) · 2 toluene (1).<sup>[9]</sup> In the high-temperature limit, the effective

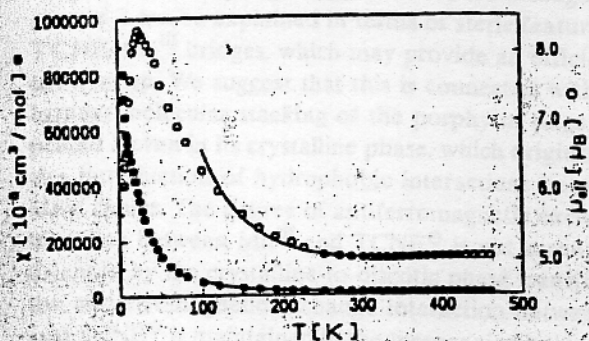


Fig. 3. Molar susceptibilities (●) and effective magnetic moments (○) in the temperature range 5–460 K for compound 2.

magnetic moment is consistent with the spin-only value of two independent ( $S = 2$ ;  $S = 1/2$ ) sublattices ( $\mu_{\text{eff}} = 5.2 \mu_B$  per pair). The experimental  $\mu_{\text{eff}}$  values were calculated based on a composition involving two toluene molecules per Mn<sup>III</sup>. Therefore, the magnetic behavior in the high temperature region—as well as the results of the elemental analysis—confirm the suggested formulas, including the presence of two solvent molecules per Mn<sup>III</sup>. On cooling, the effective magnetic moment  $\mu_{\text{eff}}$  decreases and reaches a minimum around  $T_{\text{min}} = 320$  K for 2, = 170 K for 3 and = 130 K for 4 and then increases when  $T$  is lowered further to maxima at = 25.0 K, 16.5 K, and 16.5 K for 2, 3, and 4, respectively. The maximum values of  $\mu_{\text{eff}} = 8.3 \mu_B$  for 2,  $10.3 \mu_B$  for 3, and  $8.6 \mu_B$  for 4 exceed the spin-only value of  $5.9 \mu_B$  expected even for a ferromagnetic coupled ( $S = 2$ ;  $S = 1/2$ )-unit. This result clearly indicates the presence of long-range magnetic order in the solids. It should be pointed out that, in the case of the mesogenic compound 2, the crystalline-to-discotic phase transition is not connected with a discontinuity in the  $\chi(T)$  curve.

The significant temperature dependence of  $\mu_{\text{eff}}$  as observed for 2, 3, and 4 is characteristic for 1D ferrimagnetic chains, which generally exhibit a so-called irregular spin-state structure. As a consequence of this irregularity, a minimum in the  $\mu_{\text{eff}}(T)$  curve at  $T_{\text{min}}$  was observed. This minimum is connected with a short-range ordered state: spins of adjacent magnetic centers are antiparallel without any correlation between neighboring Mn<sup>III</sup>/TCNE<sup>⊖</sup> pairs. At higher temperatures, the effective magnetic moment

increases and tends to the paramagnetic limit. At lower temperatures, the increase of  $\mu_{\text{eff}}$  is due to the increasing correlation length within the ferrimagnetic chain. Above  $T_{\text{min}}$ , the susceptibility can be fitted by the Curie–Weiss expression  $\chi \propto C/(T-\theta)$  with  $\theta = -10$  K for 2,  $-12$  K for 3, and  $-16$  K for 4.

Several approaches to a quantitative description of the temperature dependence of the magnetic susceptibility of one-dimensional ferrimagnetic chains, in which two kinds of spin centers  $S_A$  and  $S_B$  alternate regularly, have been presented in the literature, although most of them are rather poor approximations if the magnitude of either  $S_A$  or  $S_B$  is large. For such kinds of one-dimensional ferrimagnetic ( $S_A, S_B$ ) chains, the analytical expression Equation 1 for the temperature dependence of the magnetic susceptibility  $\chi(T)$  was proposed by Drillon et al.<sup>[17]</sup>

$$\chi = \frac{N_1 g^2 \mu_B^2}{3kT} \left( g^2 \frac{1+u}{1-u} + \delta^2 \frac{1-u}{1+u} \right) \quad (1)$$

$$g = (g_A^{\text{eff}} + g_B^{\text{eff}})/2 \quad (2)$$

$$\delta = (g_A^{\text{eff}} - g_B^{\text{eff}})/2 \quad (3)$$

$$u = \coth(J_{\text{intra}}^{\text{eff}}/kT) - (kT/J_{\text{intra}}^{\text{eff}}) \quad (4)$$

$$J_{\text{intra}}^{\text{eff}} = J_{\text{intra}} [S_A(S_A + 1)S_B(S_B + 1)]^{1/2} \quad (5)$$

$$g_A^{\text{eff}} = g_A [S_A(S_A + 1)]^{1/2} \quad (6)$$

$$g_B^{\text{eff}} = g_B [S_B(S_B + 1)]^{1/2} \quad (7)$$

Equation 1 leads to a linear correlation (Eq. 8) between  $J_{\text{intra}}$  (based on the Hamiltonian  $\mathcal{H} = -JS_{i+1}$ ) and the temperature  $T_{\text{min}}$ . A similar expression was derived by Seiden.<sup>[18]</sup>

$$T_{\text{min}} = 1.84 J_{\text{intra}}/k \quad (8)$$

Consequently, although it is an approximation, Equation 1 can be used to describe the strength of the intrachain coupling in a phenomenological way. The best parameters obtained fitting the  $\chi(T)$  data above 100 K were  $g = 2.19$ ,  $J_{\text{intra}} = -123.7 \text{ cm}^{-1}$  for 2,  $g = 2.25$ ,  $J_{\text{intra}} = -53.1 \text{ cm}^{-1}$  for 3, and  $g = 2.22$ ,  $J_{\text{intra}} = -47.1 \text{ cm}^{-1}$  for 4. The solid line in Figure 3 originates from this fit. Alternatively, Equation 8 can be used to estimate the intrachain coupling constant  $J_{\text{intra}}$  based on the experimental values  $T_{\text{min}}$ . The calculated values  $J_{\text{intra}}$  for 2, 3, and 4 are given in Table 1, including additionally the data for compound 1.<sup>[9]</sup>

The magnitude of  $J_{\text{intra}}$  can be regarded as a consequence of electronic and steric properties of the TCNE<sup>⊖</sup>-Mn<sup>III</sup> bridges. The decrease in  $J_{\text{intra}}$  on going from 1 to 3 and 4 is probably due to the increasing electron density at the Mn<sup>III</sup> atom, which results from the substitution, in the order 1, 3, and 4. Generally, addition of electron-donating groups leads to an increase of electron density at the metal ion

Table 1.  $T_c$ ,  $T_{min}$ , and calculated  $J_{intra}$  values from Equations 1 and 8.

Compound	$T_{min}$ [K]	$J_{intra}$ (Eq. 1) [cm <sup>-1</sup> ]	$J_{intra}$ (Eq. 8) [cm <sup>-1</sup> ]	$T_c$ [K]
2	320	-123.7	-121	21.4
3	170	-53.1	-64	7.9
4	130	-47.1	-49	5.7
[113]	310	-	-	18

incorporated in the porphyrine chelate and consequently to an increased Mn<sup>III</sup>-TCNE<sup>⊖</sup> distance. If one considers only the electronic properties of the Mn<sup>III</sup> ions, the  $J_{intra}$  value of complexes 2 and 4 should be comparable. Most probably, the relatively high  $J_{intra}$  value for the mesogenic compound 2 can be explained in terms of steric features of the TCNE-Mn<sup>III</sup> bridges, which may provide an efficient orbital overlap. We suggest that this is connected with the columnar molecular stacking of the porphyrin rings of compound 2 even in its crystalline phase, which originates from the introduction of hydrophobic interactions between the alkyl chains. The degree of antiferromagnetic exchange interaction between Mn<sup>III</sup> and TCNE<sup>⊖</sup> is not essentially influenced by the crystalline-to-discotic phase transition, i.e., the antiferromagnetic exchange interaction between Mn<sup>III</sup> and TCNE<sup>⊖</sup> is maintained in the mesogenic phase.

In order to confirm the onset of a long-range magnetic order in the Mn<sup>III</sup>-porphyrins, we carried out AC susceptibility measurements on 2, 3, and 4. The temperature dependence of the in-phase  $\chi'$  and out-of-phase  $\chi''$  components of the complex magnetic susceptibility data in zero static field ( $\nu_{ac} = 111$  Hz,  $H_{ac} = 10$  Oe) of 2 are displayed in Figure 4.

The most important feature of the AC measurements presented is the onset of a rather large out-of-phase  $\chi''(T)$  component at zero static magnetic field with maxima at 21 K for 2, 7.5 K for 3, and 5.1 K for 4 (Fig. 4). The  $\chi'(T)$  curves exhibit relatively sharp maxima at 21.4, 7.9, and

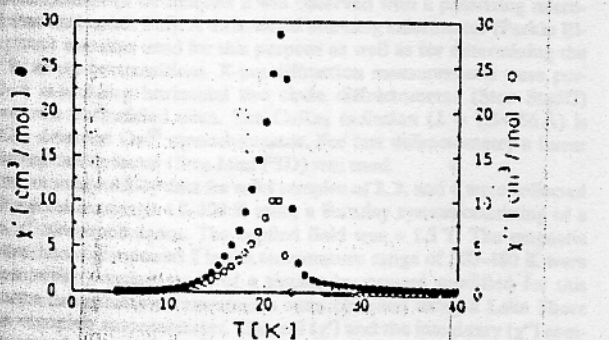


Fig. 4. Temperature dependence of  $\chi'$  (●) and  $\chi''$  (○) AC susceptibility components for 2 in the temperature region 4–40 K obtained at zero external magnetic field;  $H_{ac} = 111$  Hz.

5.7 K for 2, 3, and 4, respectively. These results clearly indicate the presence of net magnetic moments at zero applied field in the complexes. The relatively high values of  $\chi''$  with respect to the corresponding magnitude of  $\chi'$  give strong

evidence for the existence of a 3d-ferrimagnetic state below 21.4 K for 2, 7.9 K for 3, and 5.7 K for 4. The in-phase susceptibility values  $\chi'(T)$  in the temperature region  $T > 70$  K coincide with those obtained from magnetic susceptibility measurements at 1.5 K. The decrease in  $\chi'(T)$  below the maxima is most probably connected with the increasing domain wall stiffness with decreasing temperature, which is common in molecular-based ferromagnets exhibiting anisotropy and low magnetic density. Such systems can be compared with conventional ferromagnets, and domain wall mobility is almost immobile so that  $\chi'$  should drop rapidly from a maximum value immediately below  $T_c$ .<sup>[19]</sup> It should be mentioned that a similar situation was reported for  $V(\text{TCNE})_2 \cdot 1/2 \text{CH}_2\text{Cl}_2$ .

For compound 2, we carried out some additional experiments, varying the frequency  $\nu_{ac}$  and the amplitude  $H_{ac}$  of the alternating field as well as the strength of the static field (Figs. 5 and 6). As expected, the temperature of the maximum value of the  $\chi'(T)$  for 2 is only slightly influenced by the frequency  $\nu_{ac}$  and is not affected by the amplitude  $H_{ac}$ . The magnitude of this  $\chi'(T)$  maximum decreases with increasing static magnetic field (100 Oe), whereas the corresponding temperature remains unchanged (Fig. 5).

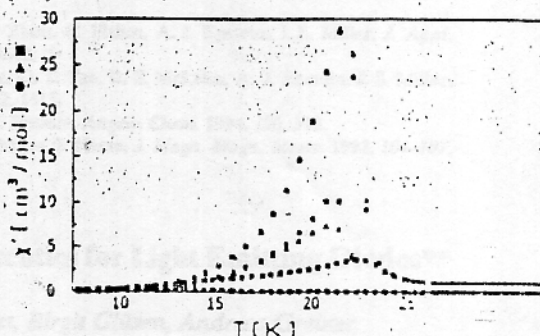


Fig. 5. Temperature dependence of the  $\chi'$  (●) ( $\nu_{ac} = 10$  Hz; ○) ( $\nu_{ac} = 1$  Hz) and  $\chi''$  AC susceptibility component (○) ( $\nu_{ac} = 10$  Hz; ○) ( $\nu_{ac} = 1$  Hz) for compound 2 in the temperature region 7.5–27.5 K at zero static magnetic field and applied static field (■) ( $\chi'$ ; □) ( $\chi''$ ); 100 Oe;  $\nu_{ac} = 111$  Hz).

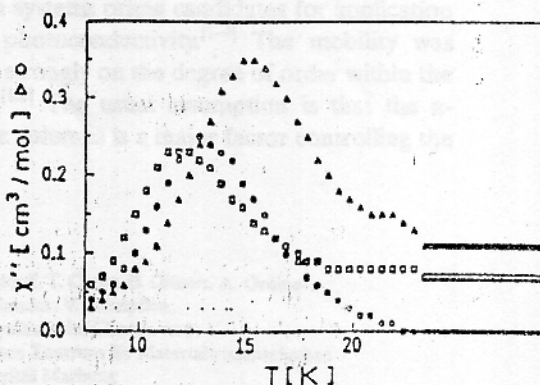


Fig. 6. Temperature dependence of the  $\chi''$  AC susceptibility component for compound 2 in the temperature region 7.5–27.5 K obtained at  $H_{ac} = 10$  Oe and varying  $\nu_{ac}$  (□) ( $\nu_{ac} = 33$  Hz; ○) ( $\nu_{ac} = 111$  Hz; △) ( $\nu_{ac} = 333$  Hz) and applying a static field of  $H_{stat} = 100$  Oe.

static magnetic field of 100 Oe is applied, the  $\chi''$  signal at 21 K decreases and appears now as a shoulder in the  $\chi''(T)$  curve (Fig. 6). The weak  $\chi''(T)$  maximum at  $\approx 12$  K observed in the case  $H_{\text{stat}} = 100$  Oe is most probably connected with a transition from a ferrimagnetic ordered state into a reentrant spin glass, as reported for  $(\text{Fe}_{0.65}\text{Ni}_{0.25})_{1-x}\text{Mn}_x$ .<sup>[22]</sup> In accordance with this interpretation, we observed an increase of magnitude as well as temperature of this  $\chi''(T)$  signal with increasing frequency  $\nu_{\text{ac}}$ .

From our AC susceptibility measurements, we can estimate the critical temperatures  $T_c$  (corresponding to the maximum of the  $\chi''(T)$  curve) as 21.4 K for 2, 7.9 K for 3, and 5.7 K for 4 (Table 1). For all compounds 1–4, the  $T_c$  values correlate strongly with the degree of intrachain coupling. Consequently, the mesogenic compound 2 exhibits a slightly higher  $T_c$  value than reported for 1.

## Experimental

The ligands  $(\text{CH}_3)_4\text{TPP}$ ,  $(\text{OCH}_3)_4\text{TPP}$ , and  $(\text{OC}_{12}\text{H}_{25})_4\text{TPP}$  were synthesized as described by Thomas and Martell [14]. In contrast to the results published by Kugimiya and Takemura [10], our X-ray investigations could not confirm mesogenic behavior for the free porphyrin ligand  $(\text{OC}_{12}\text{H}_{25})_4\text{TPP}$ ,  $[\text{Mn}^{\text{III}}((\text{OC}_{12}\text{H}_{25})_4\text{TPP})](\text{TCNE}) \cdot 2$  toluene (2),  $[\text{Mn}^{\text{III}}((\text{CH}_3)_4\text{TPP})](\text{TCNE}) \cdot 2$  toluene (3), and  $[\text{Mn}^{\text{III}}((\text{OCH}_3)_4\text{TPP})](\text{TCNE}) \cdot 2$  toluene (4) were prepared following essentially the method reported by Summerville et al. [8].

It should be mentioned, that—in contrast to the general method presented for the non-mesogenic compounds— $[\text{Mn}^{\text{III}}((\text{OC}_{12}\text{H}_{25})_4\text{TPP})]\text{Cl}$  was purified by washing the crude product with an ether–water (1:1) mixture, isolating the organic layer, and evaporating the solvent. Moreover, the resulting product,  $[\text{Mn}^{\text{III}}((\text{OC}_{12}\text{H}_{25})_4\text{TPP})](\text{TCNE}) \cdot 2$  toluene (2), was found to be soluble in toluene and could be isolated after evaporating this solvent under reduced pressure and washing the resulting product with methanol.

Analytical data (including toluene as solvent): Calcd for  $\text{C}_{112}\text{H}_{140}\text{N}_8\text{Mn}$  (2): C 78.33%, H 8.22%, N 6.52%; found: C 78.56%, H 8.15%, N 6.63%. Calcd for  $\text{C}_{64}\text{H}_{52}\text{N}_8\text{Mn}$  (3): C 78.82%, H 5.06%, N 10.81%; found: C 78.73%, H 5.12%, N 10.73%. Calcd for  $\text{C}_{64}\text{H}_{52}\text{N}_8\text{O}_4\text{Mn}$  (4): C 74.24%, H 4.76%, N 10.18%; found: C 74.01%, H 4.81%, N 10.19%. The likewise sharp  $\nu_{\text{C-N}}$  absorption (Nujol) at 2143 (m) and 2196 (cm)  $\text{cm}^{-1}$  in 2, 3, and 4 indicates the presence of bound TCNE<sup>9</sup>.

The phase behavior of complex 2 was observed with a polarizing microscope (Leitz Orthoplan Pol). A differential scanning calorimeter (Perkin Elmer DSC-2C) was also used for this purpose as well as for determining the enthalpies of phase transitions. X-ray diffraction measurements were performed by a focusing horizontal two circle diffractometer (Stoe Stadit) equipped with a modified oven. The  $\text{CuK}\alpha_1$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) is focused by a curved  $\text{Ge}^{\text{III}}$  monochromator. For fast diffractometry a linear position sensitive detector (Stoe Mini PSD) was used.

Magnetic susceptibility data for solid samples of 2, 3, and 4 were collected in the temperature range 4.2–300 K using a Faraday system consisting of a CAHN D-200 microbalance. The applied field was  $\approx 1.5$  T. The magnetic susceptibilities of compound 2 in the temperature range of 300–480 K were measured in the heating mode of a similar instrument modified for this range. AC susceptibility measurements were obtained using a Lake Shore mutual inductance susceptometer. The real ( $\chi'$ ) and the imaginary ( $\chi''$ ) components of the complex susceptibility were recorded with increasing temperature, beginning from 4.2 K. The results presented here were obtained for the frequency  $\nu_{\text{ac}}$  and the amplitude  $H_{\text{ac}}$  of the excited magnetic field equal to 111 Hz and 10 Oe, respectively, at zero static magnetic field. For complex 2 we carried out some additional experiments varying frequency ( $\nu_{\text{ac}} = 33, 111, 666$  Hz) and amplitude of the alternating field  $H_{\text{ac}}(1; 10 \text{ Oe})$  as well as the strength of the static field ( $H_{\text{stat}} = 0, 100 \text{ Oe}$ ).

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## Columnar Discotics for Light Emitting Diodes\*\*

By Thomas Christ, Birgit Glösen, Andreas Greiner, Andreas Kettner, Roland Sander, Volker Stümpflen, Vladimir Tsukruk, and Joachim H. Wendorff\*

It has recently been demonstrated that columnar discotic systems display unusually large charge carrier mobilities, which make such systems prime candidates for application in the area of photoconductivity.<sup>[1–4]</sup> The mobility was found to depend strongly on the degree of order within the columnar phase.<sup>[1,3]</sup> The usual assumption is that the  $\pi$ -overlap along the columns is a major factor controlling the

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