Liquid Crystals

Thermotropic Properties and Molecular Packing of Discotic Tristriazolotriazines with Rigid Substituents

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Dedicated to Professor Rudolf Zentel on the occasion of his 60th birthday

Abstract: Tristriazolotriazines with a threefold dialkoxyaryl substitution have been prepared by Huisgen reaction of cyanuric chloride and the corresponding tetrazoles. Although these dyes show a negative or inverted solvatochromism of the UV/Vis absorption, their fluorescence is strongly positive solvatochromic. These discotic fluorophores are also emissive in their solid state and in their broad liquid-crystalline mesophase. The structural study indicates that the thermotropic properties and organization of these systems can be

Introduction

Thermotropic liquid crystals (LC) form an important category of soft matter, molecular order and dynamics of which are intermediate between the isotropic fluid and that of a crystal.^[1,2] Compounds forming thermotropic mesophases are generally composed of a rigid core and flexible side chains with a carefully balanced size ratio. The core usually consists of an elongated, rod-like unit including aromatic rings. With flexible aliphatic chains, these mesogenes form calamitic liquid crystals (LCs). Bending the linear core results in banana-shaped biaxial molecules.^[4] Molecules with a two-dimensional, disc-like core form another class of thermotropic LCs. Commonly, discotic LCs have a large $\pi\text{-}conjugated$ aromatic system substituted with aliphatic side chains with typically high symmetry.^[1,4] The core is usually an extended polycyclic aromatic hydrocarbon, such as triphenylene or hexabenzocoronene, but star-like compounds consisting of a small central ring and three-to-six $\pi\text{-}$ conjugated arms can also meet the steric requirements for the

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well tuned by the steric demand of the aryl groups. Depending on the substituents, the compounds showed either a pure crystalline phase or a highly complex helical superstructure with a characteristic liquid-crystalline phase at elevated temperatures. Changing the steric demand of the attached aryls allowed controlling the discs arrangement within the columnar helix, which is of great importance for the molecular orbital overlap.

formation of liquid crystals.^[5,6] Discotic LCs of this type are known to self-assemble into columnar superstructures driven by π stacking of the core and local phase separation between the aromatic center and the aliphatic rim. Due to an efficient π overlap of neighboring molecules in columnar aggregates, these materials are enabled to one-dimensional charge-carrier transport,^[4] which qualifies these discotic LCs as semiconducting materials in organic-field-effect transistors and photovoltaics.^[7] To ensure high mobilities of the charge carriers, a defectfree and close intracolumnar packing of the molecules are an essential prerequisite. As an additional factor, the arrangement of the building blocks towards each other plays a role for the molecular orbital overlap and thus for the electron tunneling between two adjacent discs. This local intermolecular organization is controllable by the molecular design of the shape and symmetry of the aromatic core, as well as the architecture and functionality of the substituents.^[25b]

The vast majority of semiconducting discotic LCs are based on electron-rich polycyclic aromatic hydrocarbons, such as triphenylene,^[8] hexabenzocoronene, and even larger π systems with a strong preference for hole-conduction.^[9] Discotic LCs with an n-type, electron-transporting core are still rather scarce.^[10] Functionalization of intrinsically p-type acenes with electron-withdrawing groups (EWGs) is a common strategy to realize useful n-type materials.^[11] Similarly, the exchange of benzene rings with electron-deficient heterocycles proved to be a successful route. For example, hexa-azatriphenylenes^[12] are of the most promising candidates for electron-transporting semiconductors. This core is composed of three electron-deficient pyrazine units. A closely related polycyclic molecule was obtained by a (formal) cyclocondensation of three 1,2,4-triazoles to tris[1,2,4]triazolo[1,3,5]triazine, a heterocyclic system

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with C_{3h} symmetry.^[13] Though known for over a century,^[14] this disc-shaped molecule has only recently been recognized as a core for discotic LCs.^[15,16] The synthesis of alkoxyaryl-tristriazolotriazines follows Huisgens et al. procedure: condensation of three 5-phenyltetrazoles with cyanuric chloride followed by ring transformation leads to 3,7,11-trisubstituted tri-[1, 2, 4]triazolo[4,3-a:4,3-c:4,3-e][1,3,5]triazines (TTTs).^[17] Six alkoxy side chains on the rim guarantee excellent solubility in common solvents. These discotic molecules with propeller-like arranged aryl groups form broad thermotropic mesophases with a hexagonal columnar phase in the liquid-crystalline state and highly complex helical superstructures in their crystallinelike phase. For these model compounds, it has been proven that the phase formation, intermolecular packing, and helical packing can be precisely tuned by the steric demand of the aryl groups persisting a close π -stacking distance.

Herein, we present the synthesis of three star-shaped TTTs 1-3 with a threefold dialkoxyaryl-substitution.^[6] The size of the rigid triaryl-TTT is gradually increased, from a simple triphenyl substitution to tris(β -naphthyl) and tris(4-biphenylyl).

Results and Discussion

Synthesis

Huisgens et al. method^[17] is currently the only synthetic approach to TTTs, which allows to obtain this tetracyclic system with carbon-based substituents. With minor modifications of the original procedure, TTTs **1–3** were obtained by threefold acylation of 5-aryltetrazoles **4–6** with cyanuric chloride **7**. A thermal elimination of nitrogen from an acyltetrazole unit led to a 1,5-dipole that cyclizes to a 1,2,4-triazole annulated to the central 1,3,5-triazine (Scheme 1). Simple triphenyl-TTT is a solid



Scheme 1. Synthesis of TTTs. Reagents and conditions: i) collidine, xylenes, RT–80 °C. 1: R=3,4-dioctyloxyphenyl: 79%; 2: R=5,6-dioctyloxynaphthalen-2-yl: 72%; 3: R=3',4'-didecyloxybiphenyl-4-yl: 52%.

with a high melting point (m.p. 310 °C).^[17] To obtain discotic molecules with the ability to form thermotropic mesophases, a substitution of the triphenyl-TTT with two or three flexible side chains on terminal positions of all benzene rings is required.

The synthesis of all required tetrazoles starts with the alkylation of catechols. Addition of hydrazoic acid to benzonitrile **9** gave 3,4-dioctyloxyphenyltetrazole **4** in 71% yield (Scheme 2). Similarly, the synthesis of naphthalenyl tetrazole **5** starts with alkylation of 2-bromonaphthalenediol **10**.^[18] A Rosenmund–von Braun reaction gave nitrile **12** (46%), which was converted to the tetrazole **5** (79%).



Scheme 2. Synthesis of tetrazoles **4** and **5**. Reagents and conditions: i) Br- C_8H_{17} , K_2CO_3 , DMF, 80 °C, **9**: 87%, **11**: 65%; ii) NaN₃, Et₃N×HCl, toluene, reflux, **4**: 71%, **5**: 79%; iii) CuCN, NMP, 200 °C, **12**: 46%.

A convergent strategy was chosen for the preparation of biphenyl-substituted tetrazole **6**. The final step is a Pd-catalyzed Suzuki cross-coupling reaction of iodo-phenyl tetrazole **16** and didecyloxyphenyl boronic acid **15**.^[19] lodophenyl tetrazole **16** was prepared from iodobenzoic amide^[20] and triazido chlorosilane (89%)^[21] Regarding the extension of the rigid core, the longer decyl chains were attached to catechol. *N*-Bromosuccinimide (NBS) selectively brominated the 4-position of **13** (95%; Scheme 3). A bromine/lithium exchange on **14** and subsequent treatment with tri-*iso*-propyl borate followed by hydrolysis led



Scheme 3. Synthesis of biphenyl-tetrazole 6. Reagents and conditions: i) NBS, CHCl₃, reflux 14: 95%; ii) 1) *n*BuLi, diethyl ether, -20°C; 2) B(O-*iso*-propyl)₃, -70°C-RT, HCl (2 N), 15: 77%; iii) [Pd(PPh₃)₄], K₂CO₃, glyme/water (1:1), N₂, reflux, 6: 27%.

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to the required boronic acid **15** (77%). The Pd-catalyzed coupling of **15** to tetrazole **16** gave the desired biphenylyl-tetrazole **6** in 27% yield. As described in Scheme 1, the tetrazoles **4–6** were used to obtain the TTTs **1–3**.

Optical properties

The tristriazolotriazines 1-3 are colorless solids with a good solubility in nonpolar solvents irradiated with UV, the pure compounds, as well as their solutions, emit a violet fluorescence. The optical properties of TTTs 1-3 are presented in Table 1. The maximum of the long-wavelength absorption

Table 1. Optical properties and solvatochromism.					
Entry	Solvent	λ_{\max} [nm]	logε	$\lambda F_{\rm max}$ [nm]	$\Delta ilde{v}_{ m solv}~[m cm^{-1}]$
TTT 1	cyclohexane	310	4.63	370	5231
	toluene	310	4.66	373	5448
	dichloromethane	307	4.62	389	6866
	acetonitrile	299	4.61	391	7869
	ethanol	302	4.61	395	7796
	film	327		388	4808
TTT 2	cyclohexane	327	4.53	398	5455
	toluene	327	4.63	417	6600
	dichloromethane	329	4.58	448	8074
	acetonitrile	328	4.61	459	8701
	ethanol	324	4.56	453	8789
	film	338		428	6221
TTT 3	cyclohexane	320	4.86	394	5869
	toluene	324	4.91	404	6112
	dichloromethane	322	4.85	433	7961
	acetonitrile	325	4.35	445	8297
	ethanol	322	4.70	445	8584
	film	326		422	6978

band of TTT **1** appears in the UV ($\lambda_{max} = 310$ nm, in cyclohexane) and compound TTT 2 with the larger naphthyl substituents absorbs at longer wavelengths (λ_{max} = 327 nm). Due to the twisted biphenyl linkage, the absorption spectrum of TTT 3 peaks at an intermediate position ($\lambda_{max} = 320$ nm). The fluorescence of all TTTs is separated from the absorption by large Stokes shifts increasing with the size of the π systems. Though the maxima of the fluorescence spectra of TTTs 1-3 in cyclohexane are observed in the UV, their intense emissions extend into the violet region, especially for the compounds with the naphthalenyl and biphenylyl units. Similar to the solution, TTTs 1-3 are fluorescent in the solid state. Spin-coated films were obtained from TTTs 1-3 from toluene solution on glass substrates. Compared with solution, the absorption spectra in the spin-coated films were broadened and slightly shifted to longer wavelengths, and the shift decreased with increasing core size.

An increasing polarity of the solvent affects the absorption and emission spectra. Although the absorption of TTT **1** is negatively solvatochromic ($\Delta \tilde{v}_{solv}$ -854 cm⁻¹ for cyclohexane to ethanol), TTT **2** and TTT **3** displayed a weak but inverted solvatochromism. Furthermore, their absorption spectra were significantly broadened in the polar solvents. This and the smaller absorption coefficients of TTTs **1–3** in ethanol and acetonitrile indicate an aggregation of the chromophores even in highly diluted (ca. 10^{-7} M) solution. Contrary to the negative or inverted solvatochromism of their absorption spectra, increasing solvent polarity shifted the fluorescence of all TTTs strongly to the red. The effect of enhanced solvent polarity (cyclohexane to ethanol) increased in the sequence TTT 1 ($\Delta \tilde{v}_{
m solv} =$ 1710 cm⁻¹) < TTT **3** ($\Delta \tilde{v}_{solv} = 2908 \text{ cm}^{-1}$) < TTT **2** ($\Delta \tilde{v}_{solv} =$ 3051 cm⁻¹). These C₃-symmetric, octupolar chromophores are composed of three loosely coupled dipolar π systems. The solvatochromism of the absorption spectra revealed a polar ground state of the short dialkoxyphenyltriazole segment. The inverted solvatochromism of the absorption of TTT 2 and TTT 3 can be attributed to a superposition of dipole stabilization and a significantly enhanced polarizability of the extended conjugated systems.^[22] Excitation causes an intramolecular charge transfer from the donor groups to the acceptor triazole. Accordingly, the larger conjugated systems are more dipolar and their stabilization by solvent dipoles leads to a pronounced positive solvatochromism.

Thermotropic properties

The mesomorphic properties of the three disc-like TTTs were characterized by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and wide- and small-angle X-ray scattering (WAXS and SAXS). Investigations of TTT **1**, **2**, and **3** with a polarized optical microscope indicate pseudo-focal conic fan-shaped textures by cooling ($10^{\circ}Cmin^{-1}$) the mesogenes from the isotropic liquid phase into an enantiotropic liquid-crystalline phase. These fan-shaped textures were characteristic for a discotic hexagonal columnar phase (Col_h).^[23] Slow cooling ($1^{\circ}Cmin^{-1}$) of TTT **1** and TTT **2** led to dendritic growth, a characteristic behavior of columnar liquid-crystalline phases.^[23] Figure 1 shows the observed textures of the mesophases at fast and slow cooling.



Figure 1. POM textures (crossed-polarizers) of TTTs 1–3 in the mesophase. a) TTT 1: fast cooling (10 Kmin⁻¹), 225 °C; b) TTT 1: slow cooling (1 Kmin⁻¹), 226 °C; c) TTT 2: fast cooling (10 Kmin⁻¹), 185 °C; d) TTT 3: fast cooling (10 Kmin⁻¹), 170 °C. All scale bars = 100 μ m.

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Figure 2. DSC traces (2nd cycle) of TTT **1** and TTT **2**. Heating scans: 10 Kmin⁻¹; cooling scans: TTT **1** 20 Kmin⁻¹, TTT **2** 5 Kmin⁻¹.

In accordance to the observations by POM, DSC of TTT 1 and TTT 2 reveals two phase transitions during heating, from crystalline (Cr) to columnar hexagonal (Col_h) and from Col_h to isotropic (I; Figure 2). The second DSC heating curve of TTT 1 shows an endothermic transition into a broad columnar hexagonal discotic mesophase at 100 °C and a second, less endothermic transition at 226°C into the isotropic melt. Upon cooling, the expected exothermic transitions were slightly shifted to lower temperatures ($I \rightarrow Col_h 222 \,^{\circ}C$; $Col_h \rightarrow Cr 92 \,^{\circ}C$), both transitions occur with typical transition enthalpies of $\Delta H_{\rm m} =$ 19.9 kJ mol⁻¹ and $\Delta H_c = 4.5$ kJ mol⁻¹. Similarly, TTT **2** shows two endothermic transitions in the second heating curve $(Cr \rightarrow Col_h)$ 112°C; Col_h \rightarrow I 197°C), but only one exothermic transition upon cooling (i ${\rightarrow} \text{Col}_h$ 194 $^\circ\text{C}$). The remarkably low value for the melting enthalpy (1.3 kJ mol⁻¹) and the lack of the signal for the transition into the crystalline phase (Col_h \rightarrow Cr) were attributed to a very slow crystallization of the highly viscous material. The second DSC heating curve of TTT 3 shows only one endothermic transition at T = 172 °C with a very small enthalpy of $\Delta H = 1.2 \text{ kJ mol}^{-1}$. In the cooling scan, this transition was shifted to 167 °C. Similar to TTT 2, we assume that upon fast cooling (5 Kmin⁻¹) of the viscous liquid phase, TTT **3** does not reach the thermal equilibrium, and a supercooled melt remains. The transition temperatures and enthalpy values of all DSC thermograms are given in Table 2.

Table 2. Thermal data obtained by DSC for TTTs 1–3 . T_m = transition temperature from crystalline (Cr) to hexagonal columnar phase (Col _h).					
Entry	<i>T</i> _m [°C]	ΔH [kJ mol ⁻¹]	<i>T</i> _i [°C]	$\Delta H [\text{kJ mol}^{-1}]$	
TTT 1	100	19.9	226	4.5	
TTT 2	112	1.3	197	2.5	
TTT 3	-	-	172	1.2	
T_i = transition temperature from hexagonal columnar (Col _h) to isotropic					

liquid phase; data taken from second heating curve (10 $Kmin^{-1}$).

Structural characterization

The structure investigation of the bulk supramolecular organization was performed on macroscopically aligned fibers prepared by mechanical extrusion in the viscoelastic (liquid-crystalline phase, if present) state. For the measurements, the fibers were mounted vertically toward the two dimensional detector, which collected the scattered reflections in either in the wide- or small-angle range. In our previous studies on discotic LCs, this technique provided valuable information about the molecular arrangement and order within the superstructure.^[24]

The patterns for TTT **1** and TTT **2** recorded in their liquidcrystalline phase at higher temperatures exhibit a typical hexagonal columnar organization with nontilted discs (Figure 3).



Figure 3. 2DWAXS patterns of a) TTT 1 (at 150° C); b) TTT 2 (at 140° C) recorded in their liquid crystalline phase; and c) equatorial integration for TTT 1 (reflections are assigned by Miller's indexes).

Equatorial reflections in the small-angle regime correspond to the columnar assemblies, long-range one aligned parallel to extrusion direction (fiber axis). From their positions, hexagonal unit-cell parameters for the intercolumnar arrangement with $a_{hex} = 2.61$ nm for TTT **1** and $a_{hex} = 3.08$ nm for TTT **2** were extracted. The low intensity of the 110 and 200 reflections is characteristic for the liquid-crystalline short-range order of the samples. Additionally, an amorphous halo at around $2\theta = 20^{\circ}$ suggests fluid-like, disordered alkyl substituents. Wide-angle reflections in the meridional plane were attributed to the nontilted intracolumnar packing of the molecules from which π stacking distances of 0.34 nm for TTT **1** and 0.36 nm for TTT **2** were determined. In both cases, these reflections are quite weak, confirming the low intracolumnar order in the liquid-

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crystalline phase. The inter- and intracolumnar spacings are smaller for TTT **1** due to less bulky phenyl substituents in comparison to TTT **2**. The naphthalene units hinder an approaching of TTT **2** molecules, leading to a slightly larger π -stacking distance in the liquid-crystalline phase.

Upon cooling back the compounds to their crystalline phase, the organization significantly changed as evident from a high number of new and distinct reflections indicating a highly ordered phase (Figure 4a and b). Compound TTT **1** re-



Figure 4. 2DWAXS and 2DSAXS patterns of a), c) TTT **1** and b), d) TTT **2** obtained for the crystalline phase. Off-meridional reflections related to a long-range helical organization are indicated by dashed circles in the 2DSAXS patterns.

vealed a higher crystallinity, which is in agreement with significantly larger enthalpy values of the phase transitions due to the smaller steric influence of the phenyl substituents. The $\pi\text{-}$ stacking distance of the discs decreased to 0.33 nm for TTT 1, which is quite small in comparison to other discotics,^[4] while this intracolumnar value remains unchanged for TTT 2 for both phases. Additional meridional reflections in the middle range correspond to spacings of 0.66 nm for TTT 1 and 1.80 nm for TTT 2 and might be an evidence for dimer and pentamer (1.80/0.36 nm = 5 molecules), respectively, formation in the columnar stack. In the case of the dimer, the TTT 1 molecules could be rotated by 60° towards each other leading to staggered packing, as has been already observed for C_3 symmetric discotics.^[25] For TTT 2 in the pentamer arrangement, it is assumed that the intermolecular rotation angle decreases to 24°. However, in both cases, the corresponding reflections emerge exactly on the meridional plane of the pattern instead on the typical off-meridional range. Cerius² simulations^[26] suggest that the discs might perform a slight alternating tilting of around 7° and -7° toward the columnar axis resulting in the appearance of the reflections exactly on the meridional axis of



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Figure 5. a) Schematic illustration of the dimer intracolumnar packing of TTT 1 and Cerius2 simulation for a TTT 1 dimer with b) face-to-face packing of nontilted discs; c) nontilting and 60° rotation between discs; and d) 60° rotation and tilting of $7^{\circ}/-7^{\circ}$ (meridional reflection is indicated by dashed circle).

the patterns (Figure 5 b-d). Thereby, the exact tilting direction is unclear. The simulated patterns confirm that such small molecular tilting angles still lead to pronounced meridional π stacking reflections, which are typically an evidence for nontilting. Additionally to the dimer and pentamer organization, offmeridional scattering intensities observed in the small-angle range suggest an even more complex intracolumnar packing of the disc-like molecules (Figure 4c, d). The 011 peaks are located on a scattering line, which corresponds to a spacing of 6.60 nm for TTT 1 and 5.40 nm for TTT 2 of molecules in identical positional order within the columnar stack. This suggests that not only the molecules are rotated toward each other, but that additionally the whole dimers and pentamers are twisted by 12 and $8^\circ\!,$ respectively, toward each other (schematic illustration for two dimers is given in Figure 5 a). Therefore, 20 molecules are necessary for the helical pitch for TTT 1 and 15 for TTT 2. From the reflections on the equatorial plane in the pattern, the unit cells were identified as rectangular with a = 2.40and b = 4.40 nm (Figure S7 in the Supporting Information) for TTT **1** and a = 2.80 and b = 5.10 nm for TTT **2**.

The extension of the phenyl (in TTT 1) to biphenyl (in TTT 3) substituents inhibits the formation of a liquid-crystalline phase and results only in a crystalline state or isotropic melt at high temperatures of TTT 3 as already evident from the DSC data. In contrast to TTT 1 and TTT 2, which were extruded in their soft liquid-crystalline phase resulting in pronounced macroscopic alignment of the columnar stacks in the sample, the high crystallinity of TTT 3 prevented a sufficient orientation of domains for the measurement. Therefore, the pattern of TTT 3 displays a large number of isotropic rings, which are characteristic for the crystalline nature of the structure. Based on these results, it is only possible to determine a tilted arrangement of the discs toward the columnar axis being typical for crystalline phases of disc-shaped molecules. The wide-angle meridional





Figure 6. 2D-WAXS of TTT 3 recorded at 30 °C.

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reflections correspond to the intracolumnar period of 0.42 nm, and the off-meridional broad-scattering intensities are related to the packing distance of 0.36 nm of the tilted molecules.

Conclusion

Discotic fluorophores based on the tristriazolotriazine core substituted with dialkoxyaryl groups have been prepared. The thermotropic properties and the molecular packing of these propeller-shaped compounds are controlled by the size of the aromatic substituents. Depending on the substituents, the compounds showed either a purely crystalline phase or highly complex helical superstructure, and a liquid-crystalline phase at higher temperatures. Compounds TTT 1 and TTT 2 formed liquid-crystalline phases with a hexagonal columnar structure. 2D-WAXS and -SAXS analyses of their crystalline phases imply the formation of dimers (TTT 1) and pentamers (TTT 2) with a helical arrangement including 20 or 15 molecules, respectively. The change in helical organization corresponds to a variation in molecular arrangement and in orbital overlap that is crucial for the charge-carrier hopping between discs. These compounds serve as model systems for better understanding of the design/structure relation. In future, these finding can be transferred for the optimization of discotic semiconductors with a high device performance.

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- S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hägele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel, M. Tosoni, *Angew. Chem.* 2007, *119*, 4916–4973, and references therein.
- [2] R. J. Bushby, O. R. Lozman, Curr. Opin. Colloid Interface Sci. 2002, 7, 343 54, and references therein.
- [3] a) V. Prasad, S.-W. Kang, K. A. Suresh, L. Joshi, Q. Wang, S. Kumar, J. Am. Chem. Soc. 2005, 127, 17224–17227; b) C. Tschierske, D. J. Photinos, J. Mater. Chem. 2010, 20, 4263–4294; c) J. Seltmann, K. Müller, S. Klein, M. Lehmann, Chem. Commun. 2011, 47, 6680–6682.
- [4] S. Sergeyev, W. Pisula, Y. H. Geerts, Chem. Soc. Rev. 2007, 36, 1902– 1929.
- [5] S. Kumar, Chemistry of Discotic Liquid Crystals, CRC, Boca Raton, 2011.
- [6] H. Detert, M. Lehmann, H. Meier, Materials 2010, 3, 3218–3330, and references therein.
- [7] a) W. Pisula, X. Feng, K. Müllen, *Chem. Mater.* 2011, *23*, 554–567; b) B. R. Kaafarani, *Chem. Mater.* 2011, *23*, 378–396; c) W. Pisula, A. Menon, M. Stepputat, I. Lieberwirth, U. Kolb, A. Tracz, H. Sirringhaus, T. Pakula, K. Müllen, *Adv. Mater.* 2005, *17*, 684–689; d) J. Li, M. Kastler, W. Pisula, J. W. F. Robertson, D. Wasserfallen, A. C. Grimsdale, J. Wu, K. Müllen, *Adv. Funct. Mater.* 2007, *17*, 2528–2533; e) H. N. Tsao, W. Pisula, Z. Liu, W. Osikowicz, W. R. Salaneck, K. Müllen, *Adv. Mater.* 2008, *20*, 2715–2719.
- [8] a) S. Kumar, *Liq. Cryst.* 2005, *32*, 1089–1113; b) S. Kohmoto, E. Mori, K. Kishikawa, *J. Am. Chem. Soc.* 2007, *129*, 13364–13365; c) M. H. Hoang, M. J. Cho, K. H. Kim, M. Y. Cho, J.-s. Joo, D. H. Choi, *Thin Solid Films* 2009, *518*, 501–506; d) M. G. Schwab, T. Qin, W. Pisula, A. Mavrinskiy, X. Feng, M. Baumgarten, H. Kim, F. Laquai, S. Schuh, R. Trattnig, E. J. W. List, K. Müllen, *Chem. Asian J.* 2011, *6*, 3001–3010.
- [9] a) X. Feng, W. Pisula, K. Müllen, Pure Appl. Chem. 2009, 81, 2203-2224;
 b) W. Pisula, Ž. Tomović, C. Simpson, M. Kastler, T. Pakula, K. Müllen, Chem. Mater. 2005, 17, 4296-4303; c) M. Kastler, W. Pisula, D. Wasserfallen, T. Pakula, K. Müllen, J. Am. Chem. Soc. 2005, 127, 4286-4296;
 d) X. Feng, W. Pisula, T. Kudernac, D. Wu, L. Zhi, S. De Feyter, K. Müllen, J. Am. Chem. Soc. 2009, 131, 4439-4448; e) J. M. Warman, J. Piris, W. Pisula, M. Kastler, D. Wasserfallen, K. Müllen, J. Am. Chem. Soc. 2005, 127, 14257-14262.
- [10] a) M. Kivala, W. Pisula, S. Wang, A. Mavrinskiy, J.-P. Gisselbrecht, X. Feng, K. Müllen, *Chem. Eur. J.* 2013, *19*, 8117–8128; b) Y. Avlasevich, C. Li, K. Müllen, *J. Mater. Chem.* 2010, *20*, 3814–3826; c) X. Zhan, A. Facchetti, S. Barlow, T. J. Marks, M. A. Ratner, M. R. Wasielewski, S. R. Marder, *Adv. Mater.* 2011, *23*, 268–284; d) C. Li, H. Wonneberger, *Adv. Mater.* 2012, *24*, 613–636.
- [11] a) B. Gao, L. Zhang, Q. Bai, Y. Li, J. Yang, L. Wang, New J. Chem. 2010, 34, 2735–2738; b) Z. Liang, Q. Tang, J. Liu, J. Li, F. Yan, Q. Miao, Chem. Mater. 2010, 22, 6438–6443; c) Z. Liang, Q. Tang, J. Xu, Q. Miao, Adv. Mater. 2011, 23, 1535–1539; d) L. Tan, Y. Guo, G. Zhang, Y. Yang, D. Zhang, G. Yu, W. Xu, Y. Liu, J. Mater. Chem. 2011, 21, 18042–18048; e) X.-K. Chen, L.-Y. Zou, J.-F. Guo, A.-M. Ren, J. Mater. Chem. 2012, 22, 6471–6484; f) J.-i. Nishida, H. Deno, S. Ichimura, T. Nakagawa, Y. Yamashita, J. Mater. Chem. 2012, 22, 4483–4490; g) Y. Qiao, Y. Guo, C. Yu, F. Zhang, W. Xu, Y. Liu, D. Zhu, J. Am. Chem. Soc. 2012, 134, 4084–4087; h) Y. Qiao, J. Zhang, W. Xu, D. Zhu, J. Mater. Chem. 2012, 22, 5706–5714.
- [12] a) M. Palma, J. Levin, O. Debever, Y. Geerts, M. Lehmann, P. Samorì, Soft Matter 2008, 4, 303–310; b) V. Lemaur, D. A. da Silva Filho, V. Coropceanu, M. Lehmann, Y. Geerts, J. Piris, M. G. Debije, A. M. van de Craats, K. Senthilkumar, D. Siebbeles, J. M. Warman, J.-L. Brédas, J. Cornil, J. Am. Chem. Soc. 2004, 126, 3271–3279.
- [13] V. A. Tartakovsky, A. E. Frumkin, A. M. Churakov, Y. A. Strelenko, *Russ. Chem. Bull.* 2005, *114*, 719–725.
- [14] a) K. A. Hofmann, O. Erhardt, Ber. Dtsch. Chem. Ges. 1911, 44, 2713– 2717; b) K. A. Hofmann, O. Erhardt, Ber. Dtsch. Chem. Ges. 1912, 45, 2731–2736.
- [15] a) R. Cristiano, H. Gallardo, A. J. Bortoluzzi, I. H. Bechtold, C. E. M. Campos, R. L. Longo, *Chem. Commun.* 2008, 5134–5136; b) R. Cristiano, J. Eccher, I. H. Bechtold, C. N. Tironi, A. A. Vieira, F. Molin, H. Gallardo, *Langmuir* 2012, *28*, 11590–11598.
- [16] a) S. Glang, V. Schmitt, H. Detert, Proc. 36th German Topical Meeting Liquid Crystals 2008, 125–128; b) K. Herget, D. Schollmeyer, H. Detert, Acta Crystallogr. Sect. E 2013, 69, 0365–0366; c) S. Glang, D. Borchmann, T. Rieth, H. Detert, Adv. Sci. Technol. 2012, 77, 118–123.
- [17] R. Huisgen, H. J. Sturm, M. Seidel, Chem. Ber. 1961, 94, 1555-1562.





- [18] a) H. Thielemann, Z. Chem. 1973, 13, 216–218; b) S. Archer, P. Osei-Gyimah, S. Silbering, J. Med. Chem. 1980, 23, 516–519.
- [19] a) S. A. Lang, J. Heterocycl. Chem. 1975, 12, 1143–1153; b) J. Bonnamour, C. Bolm, Chem. Eur. J. 2009, 15, 4543–4545.
- [20] I. Remsen, E. E. Reid, Am. Chem. J. 1899, 21, 284-348.
- [21] A. El-Ahl, S. Elmorsy, A. Elbeheery, Tetrahedron Lett. 1997, 38, 1257-1260.
- [22] a) J. Catalán, J. Phys. Chem. B 2009, 113, 5951–5960; b) J. Catalán, J. L. G. de Paz, C. Reichardt, J. Phys. Chem. A 2010, 114, 6226–6234; c) J. Catalán, C. Reichardt, J. Phys. Chem. A 2012, 116, 4726–4734.
- [23] I. Dierking, Textures of Liquid Crystals, Wiley-VCH, Weinheim, 2004.
- [24] W. Pisula, X. Feng, K. Müllen, Adv. Mater. 2010, 22, 3634-3649.
- [25] a) M. Peterca, M. R. Imam, C.-H. Ahn, V. S. K. Balagurusamy, D. A. Wilson, B. M. Rosen, V. Percec, *J. Am. Chem. Soc.* 2011, *133*, 2311–2328; b) X.
 Feng, V. Marcon, W. Pisula, M. R. Hansen, J. Kirkpatrick, F. Grozema, D.
 Andrienko, K. Kremer, K. Müllen, *Nat. Mater.* 2009, *8*, 421–426; c) J. Shu,
 D. Dudenko, M. Esmaeili, J. H. Park, S. R. Puniredd, J. Y. Chang, D. W.
 Breiby, W. Pisula, M. R. Hansen, *J. Am. Chem. Soc.* 2013, *135*, 11075–11086.
- [26] Molecular Simulations Inc., San Diego, 1998.

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