IR (KBr): $\tilde{\nu} = 3360$(br, s), 2945(m), 1622(s), 1553(s), 1513(s), 1412(s), 1365(w), 1328(w), 1278(m), 1244(m), 1228(m) 1186(w), 1120(w), 1103(w), 1068(w), 1030(w), 1016(w), 951(w), 918(w), 857(w), 835(w), 780(w), 718(w), 644(w), 605(w) cm^{-1}.

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[30] Crystal data for **2**: $C_{42}H_{52}N_4O_9Cd$, orthorhombic, space group $P2_12_12_1$, $a = 13.7818(9)$, $b = 15.0617(10)$, $c = 19.355(13)$ Å, $\alpha = \beta = \gamma = 90.00°$, $V = 4017.8(5)$ Å^3, $Z = 4$, $M_r = 869.28$, $\rho_{calcd} = 1.437$ Mg m^{-3}, $R_1 = 0.0436$, $wR_2 = 0.1054$, $T = 293$ K, $\mu = 0.604$ mm^{-1}, $S = 0.744$, Flack $\chi = -0.02(2)$.

[31] Crystal data for **3**: $C_{43}H_{54}N_4O_9Cd$, orthorhombic, space group $P2_12_12_1$, $a = 13.8756(8)$, $b = 15.1162(8)$, $c = 19.2999(10)$ Å, $\alpha = \beta = \gamma = 90.00°$, $V = 4048.1(4)$ Å^3, $Z = 4$, $M_r = 883.30$, $\rho_{calcd} = 1.449$ Mg m^{-3}, $R_1 = 0.0797$, $wR_2 = 0.1684$, $T = 293$ K, $\mu = 0.601$ mm^{-1}, $S = 1.227$, Flack $\chi = -0.04(4)$. The structures were solved with Direct methods using the program SHELXTL (Sheldrick, 1997).[32] All the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least-squares procedure. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The final difference Fourier map was found to be featureless. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-166932–166935. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Control of Liquid Crystallinity of Diazadibenzoperylene Dyes by Covalent and Hydrogen-Bonded Attachment of Mesogens[**]

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Frank Würthner[*]

Dedicated to Dr. Günther Seybold
on the occasion of his 60th birthday

Functional liquid crystals (LCs) with intrinsic luminescence properties are of great interest in the development of new organic materials, such as anisotropic light emitters, organic lasers, photoconductors, and in LC display technology.[1–3] In contrast to dissolving a fluorescent dye in a LC matrix, fluorescent LCs are thought not only to overcome miscibility and stability problems but also to exhibit novel enhanced optoelectronic properties. To date, only a few examples have been reported such as triphenylenes,[3a–d] benzopyrenes,[3e] hexacatenar compounds,[1a] and perylenes,[2] but the field is

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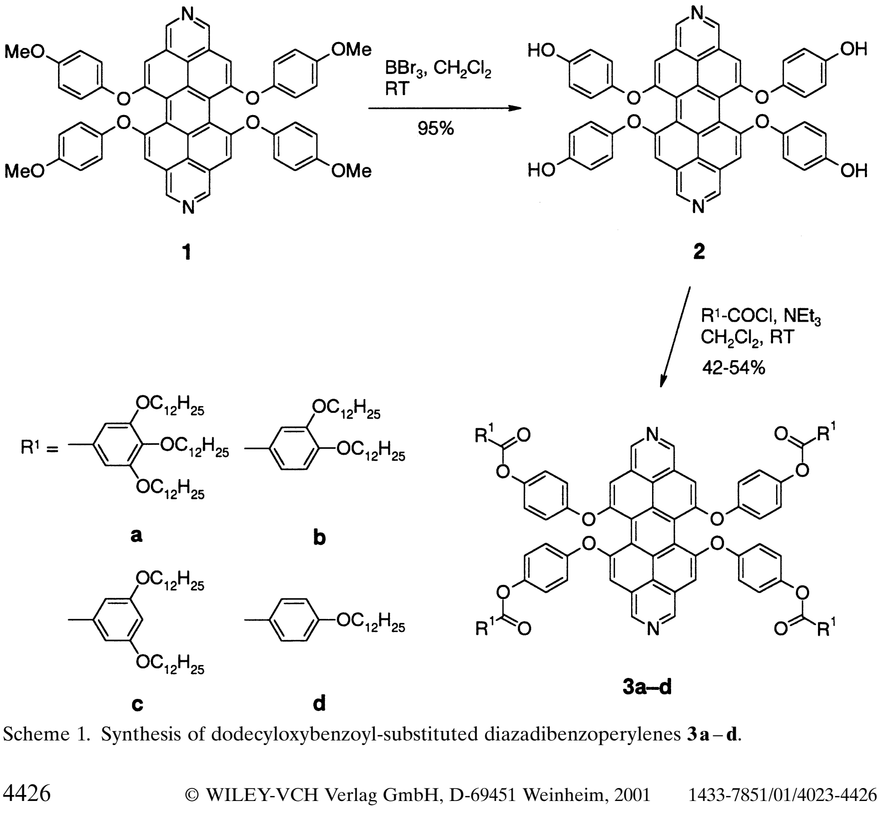
rapidly expanding. Here, we report a series of diazadibenzoperylenes **3a**–**d** that bear mesogenic dodecyloxybenzoyl substituents and aza coordination sites suited for additional control of dye packing by intermolecular interactions. All the compounds **3a**–**d** exhibit strong luminescence in solution and in the pristine (i.e. solid) states , and **3a**–**c** form thermotropic columnar liquid crystalline phases in the presence and/or absence of benzoic acids **4a**–**d**.

Cleavage of all the methoxy ethers of the diazadibenzoperylene **1**[4, 5] with BBr_3 in dichloromethane afforded tetra(*p*-hydroxyphenoxy)diazadibenzoperylene **2** in 95% isolated yield. Esterification reactions of **2** with various dodecyloxy-substituted benzoic acid chlorides in dichloromethane in the presence of triethyl amine led to the title compounds **3a**–**d** in 42–54% isolated yields (Scheme 1) after purification by chromatography.[5]

All the diazadibenzoperylenes **3a**–**d** show identical absorption and fluorescence spectra in dichloromethane, with absorption maxima at 495 nm and 464 nm, and a mirror-image fluorescence emission with maxima at 512 nm and 545 nm (Figure 1). The fluorescence quantum yields Φ_F range between 0.65 (**3c**) and 0.83 (**3b**).[6] Aggregation of the molecules in nonpolar solvents, for example methylcyclohexane (MCH), or in the solid state causes pronounced changes in the UV/Vis and fluorescence spectra. For thin films a bathochromic shift of about 10 nm and a pronounced line broadening of the UV/Vis absorption spectra is observed, which implies strong dye–dye interactions in the solid state (Figure 1). As a result of a considerable bathochromic shift of about 100 nm in the fluorescence spectra these films exhibit intense red emission in contrast to the green emission in solution. A spectral fine structure is only observed for **3a** and **b** but not for **3c** which indicates a higher molecular ordering for **3a**, **b** (Figure 1).



Scheme 1. Synthesis of dodecyloxybenzoyl-substituted diazadibenzoperylenes **3a**–**d**.

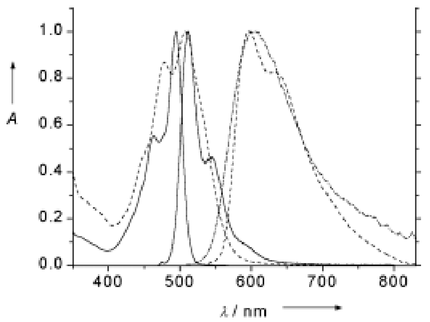


Figure 1. UV/Vis absorption and fluorescence spectra of **3b** in dichloromethane (——) and as thin film (----) on a quartz substrate and film emission spectrum of **3c** (•–•–).

The thermotropic properties of **3a**–**d** were investigated by optical polarization microscopy (OPM) and differential scanning calorimetry (DSC). Phase-transition temperatures and associated enthalpy values for compounds **3a**–**d** are given in Table 1. **3d** with only four dodecyloxy chains, melts at 249 °C and crystallizes upon cooling. No LC phase was found for this compound. Compound **3c** which bears (3,5-didodecyloxy)-benzoyl substituents exhibits an unexpected thermotropic behavior. The viscosity of a completely amorphous film of **3c** gradually decrease when the compound is heated and neither a melting point nor a glass transition was observed by OPM and DSC. In contrast, **3b** and **3a** bearing four (3,4-didodecyloxy)- and (3,4,5-tridodecyloxy)benzoyl substituents, respectively, are liquid crystalline from room temperature to their clearing points at 177 °C (**3b**) and 174 °C (**3a**).[7] On slow cooling from the isotropic liquid state large spherulitic textures (ca. 100 μm) can be observed at crossed polarizers by OPM that are characteristic for columnar LC phases (Figure 2a).[8]

Table 1. Phase transition temperatures T [°C] and transition enthalpies ΔH_t [kJ mol^{-1}] (in parentheses) for diazadibenzoperylenes **3a**–**d**.[a–c]

Compound	T [°C] (ΔH_t [kJ mol^{-1}])
3a	Col 174 (16.3) I
3b	Col 177 (27.3) I
3c	–
3d	Cr 249 (36.5) I

[a] Col = columnar mesophase; [b] I = isotropic liquid; [c] Cr = crystalline solid.

The X-ray crystal structure of a closely related *N*,*N*′-dibutylated diazadibenzoperylene revealed a twisting of the central six-membered ring of the aromatic diazadibenzoperylene backbone by 25°, because of the electrostatic repulsion of the oxygen atoms of the phenoxy substituents.[4] This twisting leads to a propeller-like arrangement of the phenoxy substituents in contrast to most tradi-

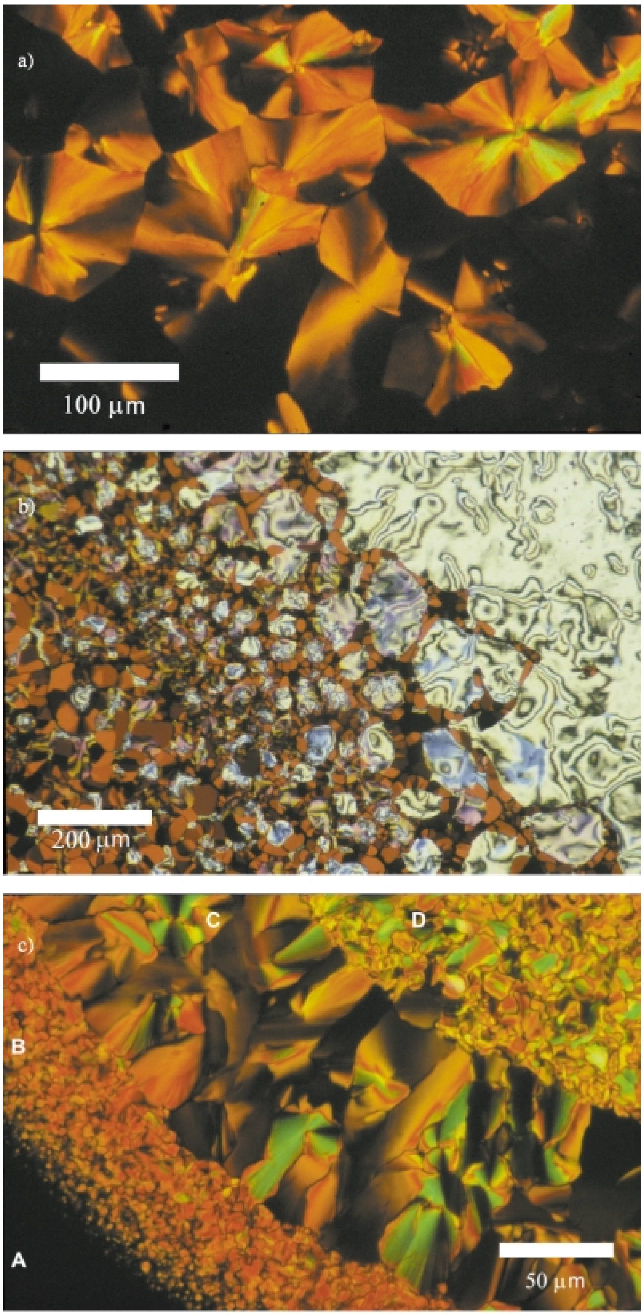
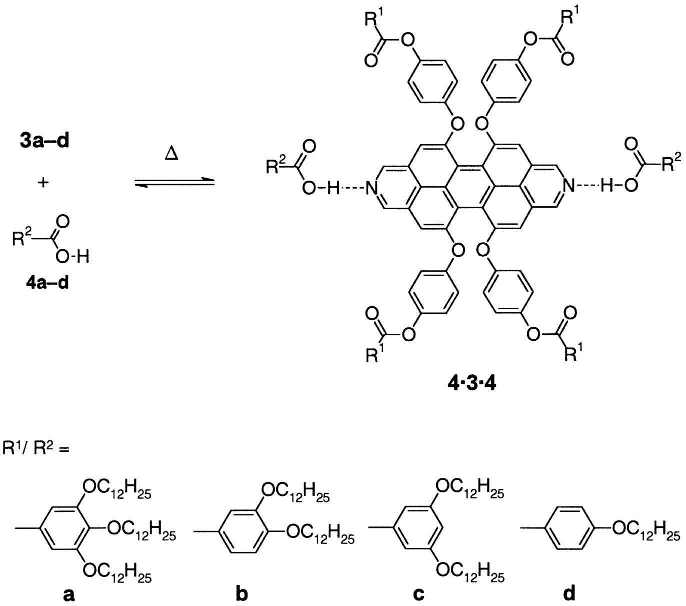


Figure 2. Optical micrographs of the textures of a) the columnar mesophase of **3a** obtained by cooling from the isotropic melt to room temperature; b) the contact region of a melting preparation of the columnar mesogen **3a** and the calamitic mesogen **4d** (top right corner); c) the contact region of a melting preparation of **3c** and **4c**, showing amorphous **3c** (A); a region rich in **3c** (B); complex [**4c** · **3c** · **4c**] (C), and a region with a lower content of **3c** (D). All micrographs were taken at crossed polarizers.

tional columnar mesogens[8] which exhibit disclike central units. Nevertheless, a number of molecules were recently reported that lack a flat core but that are capable of forming columnar mesophases. Here, the main driving force is ascribed to microsegregation,[9] which also plays the crucial role in the formation of columnar mesophases of compounds **3a**, **b** by segregation of the polar diazadibenzoperylene cores from the nonpolar dodecyl chains.

The columnar nature of the mesophase of **3b** was confirmed by X-ray diffraction (XRD) and assigned to a columnar rectangular disordered (Col_{rd}) LC phase with four sharp reflections in the small-angle region at $2\vartheta = 2.04°$, $2.57°$, $4.08°$, and $8.83°$, and a halo in the wide-angle region of the diffractogram.[10] XRD also confirmed the crystalline state of **3d** (abundant sharp reflections) and the amorphous nature of **3c** (only a diffuse reflection at $2\vartheta = 2.73°$ corresponding to 32.3 Å which is about the size of an individual molecule, and a halo in the wide-angle region around $2\vartheta = 20°$).

Compounds **3a** – **d** are distinguished from other mesogens by a unique combination of functionality (optical and redox)[4] and diaza receptor sites suitable for additional control of the supramolecular organization through coordination to carboxylic acid or Lewis-acidic binding partners (e.g. metal ions).[11–13] Here, we will concentrate on hydrogen-bonded complexes between diazadibenzoperylenes **3a** – **d** and the different dodecyloxy-substituted benzoic acids **4a** – **d** (Scheme 2).[12]



Scheme 2. Complex formation between substituted benzoic acids **4a** – **d** and a diazadibenzoperylene **3a** – **d** through hydrogen bonding by melting both compounds together between glass slides or by evaporation of a 1:2 stoichiometric solution of the two components.

For this purpose contact melting preparations were made by melting first a diazadibenzoperylene **3a** – **d** and then a benzoic acid **4a** – **d** between glass slides to give a contact region with a gradient in stoichiometry of the two components. Investigation of the phase behavior of these preparations by repeated heating – cooling cycles on a hot-stage OPM at crossed polarizers revealed crystallinity for all complexes between **3d** and **4a** – **d**, and liquid crystallinity for all complexes formed between **3a**, **b** and **4a** – **d**. For all 1:2 complexes [**4a** – **d** · **3a**, **b** · **4a** – **d**] we observed a decrease in the clearing points between 10 and 30 K with respect to the pure compounds **3a**, **b**. This indicates a destabilization of the columnar mesophases by addition of the benzoic acids which disturb the columnar organization of the mesogenic dyes

3a, **b**. When the calamitic mesogenic benzoic acid **4d** is applied especially beautiful transitions of the mesophases are observed in the contact regions with **3a**, **b** (Figure 2b). Remarkably, all the benzoic acids **4a**–**d** were able to induce columnar LC phases upon coordination to the formerly amorphous diaza ligand **3c** giving rise to well-pronounced textures in the boundary regions of the contact melting preparations. An optical micrograph taken at crossed polarizers for complexation of **3c** with **4c** is depicted in Figure 2c. The left bottom corner (A; the black area), shows amorphous pure **3c**, and the region (B) exhibits small textures which we attribute to an intermediate phase between **3c** and **4c**, rich in **3c**. In the middle region (C) well-pronounced and large textures of complex [**4c**·**3c**·**4c**] with the correct 1:2 stoichiometry can be observed which exhibit a sharp clearing transition at 116 °C. Region (D) has a low **3c** content and the textures become smaller. The same textures as in the middle regions of these contact melting preparations are also observed if complexes [**4a**–**d**·**3c**·**4a**–**d**] are prepared in an exact 1:2 stoichiometry from stock solutions. According to OPM all these mesophases have well-defined clearing points at 111 °C for [**4a**·**3c**·**4a**], 100 °C for [**4b**·**3c**·**4b**], 116 °C for [**4c**·**3c**·**4c**], and 94 °C for [**4d**·**3c**·**4d**] and also here no crystallization is observed upon cooling these samples to room temperature.[14]

In conclusion, we presented a new class of highly fluorescent mesogenic diazadibenzoperylenes **3a**–**c**, the morphological behavior of which could be controlled by hydrogen-bond directed coordination to carboxylic acids. In future work chiral hydrogen-bond donors and metal ions will be applied to induce chiroptical properties by means of the inherently atropisomeric backbone of **3a**–**d** and applications of these supramolecular assemblies in optoelectronics will be addressed.[15]

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[14] The lower clearing temperatures of these supramolecular LCs compared to those of the mesogenic dyes **3a**, **b** and the smaller size of the domains indicate a lower stability of these mesophases. Based on the textures a simple hexagonal or rectangular columnar ordering seems unlikely but further XRD studies are required to reveal the exact type of supramolecular organization.

[15] It is noteworthy that there is no quenching of the diazadibenzoperylene fluorescence upon hydrogen bonding to benzoic acids according to a fluorescence titration experiment in methylcyclohexane.