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Donor–Acceptor Systems

Supramolecular Liquid Crystals Based on Cyclo[8]pyrrole**

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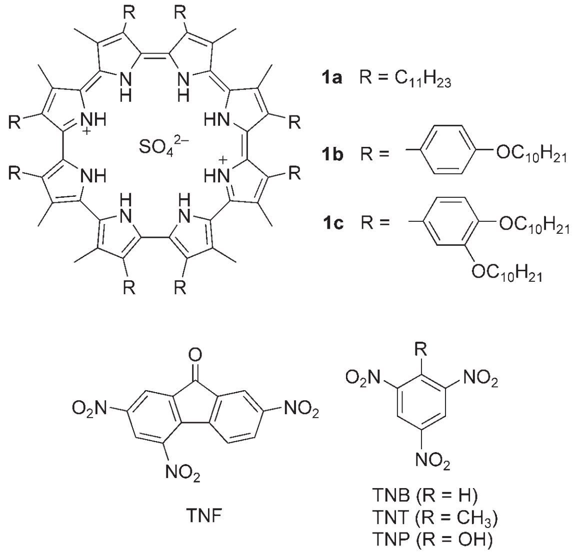
Expanded porphyrins,[1] larger analogues of naturally occurring tetrapyrrolic pigments, have attracted considerable interest in recent years because of their potential utility in areas as diverse as anticancer drug development,[2,3] nonlinear optics,[4–6] and anion recognition.[7,8] They have also seen use in the areas of cation coordination[1,9] and as test systems for the study of aromatic properties in large heteroannulenes.[1,6,10–13] As a class, expanded porphyrins possess electronic, structural, and spectral properties that are distinct from those of their far better studied porphyrin progenitors. However, in spite of these potentially attractive features, reports of liquid crystals (LCs) derived from expanded porphyrins are exceedingly rare. Indeed, we are aware of only two expanded porphyrin mesophases: both are derived from imine-linked oligopyrrolic macrocycles and neither is aromatic.[14–16] We have thus sought to produce a liquid-crystalline mesophase based on an all-carbon-linked, aromatic expanded porphyrin framework and report here the synthesis of new cyclo[8]pyrrole derivatives **1a–c** that form hexagonal columnar (Col$_h$) mesophases when combined with electron-deficient acceptors, such as trinitrofluorenone (TNF), trinitrobenzene (TNB), trinitrophenol (TNP), and trinitrotoluene (TNT). The resulting systems are structurally interesting because of the presence of hydrogen-bonded sulfate ions. Furthermore, the optical properties of the cyclo[8]pyrrole ring make the new mesophases potentially interesting materials for molecular electronic and photovoltaic applications.[17–20] Finally, the possibility of producing liquid crystallinity upon exposure to TNT makes the new cyclo[8]pyrroles described herein of interest as a possible explosives-sensing material.

A major difficulty associated with producing an all-carbon-linked expanded porphyrin liquid crystal is that most large oligopyrrolic macrocycles remain hard to make and even harder to functionalize. Furthermore, expanded porphyrin cores are very often nonplanar and highly flexible, and such characteristics are unfavorable for the formation of discotic mesophases. However, as a general rule, expanded porphyrins, like most common electron-rich aromatic species, will stabilize face-centered stacking arrangements in the presence of appropriate molecular "partners", usually electron-deficient aromatic molecules.[21–23] This appreciation led us to consider that it might be possible to generate an expanded porphyrin-based liquid-crystalline mesophase by the use of electron-donor/electron-acceptor (EDA) interactions. The advantage of this strategy, which has been exploited to produce a number of highly elegant liquid crystals in recent years,[24–26] albeit few in the porphyrin area,[27] is that it might allow liquid crystallinity to be achieved using otherwise nonmesogenic expanded porphyrin derivatives.[28]

To test the above idea we elected to focus on the use of the cyclo[8]pyrrole core. Cyclo[8]pyrroles[29] are attractive as targets in that they may be prepared in one high-yielding step from a single bipyrrolic precursor. Thus, the use of appropriately substituted bipyrroles allowed us to prepare three new cyclo[8]pyrroles, each possessing eight large substituents, namely undecyl, 4-decyloxyphenyl, or 3,4-bis(decyloxy)phenyl chains (**1a**, **1b**, and **1c**, respectively; Scheme 1). As with other cyclo[8]pyrroles prepared by our



Scheme 1. Molecular structures of cyclo[8]pyrroles **1a–c**. The sulfate ion is hydrogen-bonded inside the macrocyclic cavity.

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Supporting information for this article (full synthetic details) is available on the WWW under http://www.angewandte.org or from the author.

original procedure, **1a–c** were isolated in the form of their dihydrogen sulfate salts.[29] The sulfate anion is firmly bound within the cavity of the diprotonated macrocycle and the resulting ion pair persists both in the solid state and in solution.

In pure form, **1a–c** are not mesomorphic (Table 1). Freshly isolated **1a** slowly crystallizes on standing, whereas the other two systems can only be isolated as glassy, amorphous solids. Interestingly, in spite of its formally ionic structure, **1a** is fully miscible with typical hydrocarbon and halocarbon solvents. The lack of mesomorphic properties in **1a–c** is ascribed to an inefficient face-centered interaction between the cyclo[8]pyrrole cores. Compounds **1a–c** are, however, aromatic in a formal, Hückel-type sense and thus define large π-electron-rich surfaces. Therefore, in an effort to produce LC mesophases they were combined with a variety of electron acceptors, such as 1,3,5-trinitrobenzene (TNB), 2,4,6-trinitrotoluene (TNT), 2,4,6-trinitrophenol (TNP), and 2,4,7-trinitrofluorenone (TNF). Samples were initially prepared by dissolving stoichiometric amounts of the electron acceptor and the cyclo[8]pyrrole macrocycle in question in dichloromethane and removing the solvent by evaporation. The product was then analyzed by polarizing optical microscopy (POM), differential scanning calorimetery (DSC), and powder X-ray diffraction (XRD) methods. Relevant results are collated in Table 1 and Figure 1 and discussed for a few specific cases below.

Table 1: Thermodynamic data for cyclo[8]pyrroles **1a–c** and their adducts with electron acceptors.

Compound	Transitional properties[a]					
1a				Cr	73 [36]	I
1b				glass	ca. 150	I
1c				[glass]	ca. 50	I
1a·TNF				Col$_h$	74 [1.4]	I
1a·2TNB				Cr	86 [62]	I
1b·TNB[b]	p.s.[c]	ca. 200	Col$_h$	ca. 250–270	decomp	
1b·TNP				Col$_h$	ca. 250–270	decomp
1c·TNB				Col$_h$	171 [18]	I

[a] Transition temperatures are given in °C, and the corresponding enthalpy changes are in square brackets [ΔH in kJ mol^{-1}]. Cr: crystalline or solid state; Col$_h$: hexagonal columnar phase; I, isotropic liquid. [b] Behavior on heating: once formed, the mesophase remains unchanged on cooling to 25 °C. [c] Phase separation; for explanation see text.

One of the systems analyzed in detail consisted of an equimolar mixture of **1a** and TNF. This mixture forms a mesophase that is stable from room temperature to 74 °C. The texture obtained by POM on slow cooling of the isotropic melt shows well-developed cylindrical domains and large homeotropic zones, characteristic of a columnar hexagonal phase (Col$_h$, Figure 1). The identity of this phase was further verified by X-ray diffraction methods, as discussed in greater detail below.

Surprisingly, when **1a** is combined with TNB a crystalline material is formed, which melts into an isotropic liquid at 86 °C. The stoichiometry of this material was determined as close to 1:2, based on the analysis by microscopy of samples with varying compositions. The fact that different XRD patterns are seen for samples of **1a**·TNF and **1a**·2TNB (as well as **1a**; see the Supporting Information) provides support for the notion that materials with different inherent characteristics are produced in the presence of different electron acceptors, and that only an appropriate choice of the latter will stabilize an EDA-based mesophase.

As TNB failed to produce a mesophase when combined with **1a**, the ability of the various trinitrobenzene derivatives to act as the stabilizing electron acceptors in the case of its

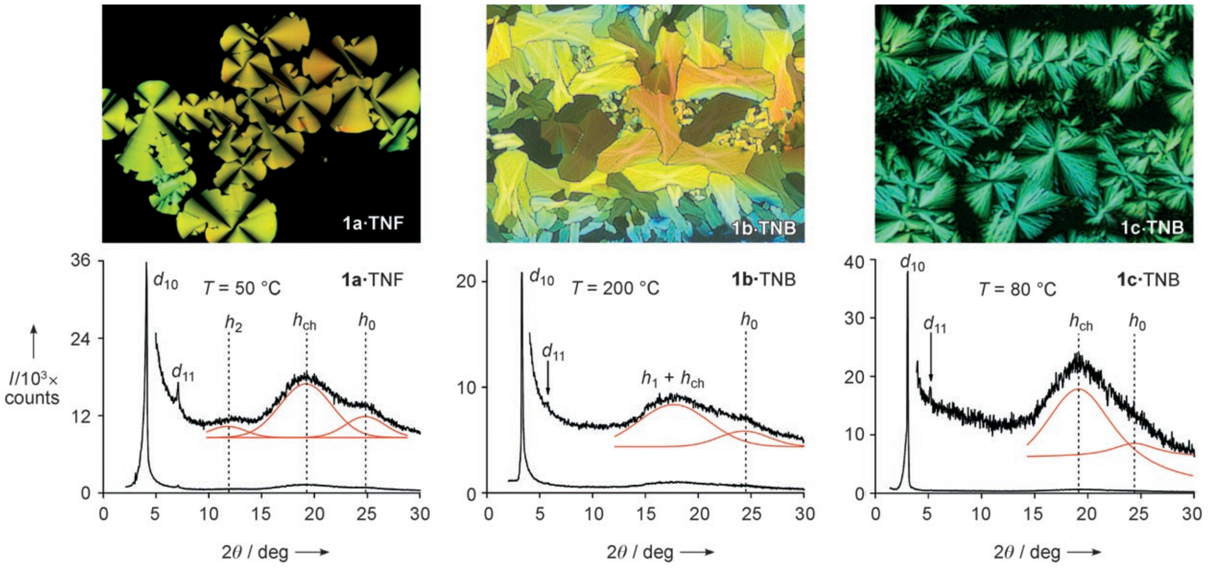

Figure 1. Characterization of liquid-crystalline adducts of cyclo[8]pyrroles with electron acceptors. POM textures (top panels) were obtained by slow cooling of the isotropic melt (**1a**·TNF, 70 °C, and **1c**·TNB, ca. 150 °C) or by fusing an equimolar mixture of the components (**1b**·TNB, 200 °C). For **1b**·TNB, the h_1 and h_{ch} peaks could not be separated by deconvolution. For a discussion of the powder XRD patterns (bottom panels) see text.

aryl-substituted congener **1b** was investigated. Here, it was found that a 1:1 mixture of **1b** and picric acid (TNP) could be isolated as a very viscous material that appeared birefringent under the polarizing microscope. When this material was heated, it gradually became more fluid; however, it would not clear into an isotropic liquid even at 250 °C. Heating the sample above this temperature led to a gradual and irreversible loss in the birefringence, presumably because of decomposition. The exceptional stability of this putative mesophase was further confirmed by DSC, which showed no phase transitions from room temperature to 250 °C, as well as by XRD, which again yielded a diffraction pattern corresponding to a $\mathrm{Col_h}$ phase (see the Supporting Information).

Replacing TNP with TNT or TNB produced mixtures with different characteristics. For example, samples of **1b**·TNB obtained from a CH_2Cl_2 solution of defined stoichiometry, appeared amorphous at room temperature. In this case, an analysis of the POM features led to the conclusion that the sample consisted of TNB microcrystals dispersed in the cyclo[8]pyrrole glass. The sample softened upon heating and then, at about 200 °C, gradually became birefringent, and again the resulting mesophase showed excellent thermal stability. Occasionally a texture was produced (Figure 1), which consisted of a mosaic polydomain containing dendritic features (fernlike) with a twofold symmetry, also characteristic of a $\mathrm{Col_h}$ phase. In the event, X-ray diffraction analysis (Figure 1) provided support for the conclusion that the mesophase obtained from **1b**·TNB is structurally very similar to that obtained in the case of **1b**·TNP. Further XRD analyses revealed that, once formed at elevated temperatures, the **1b**·TNB mesophase could be cooled down to room temperature without engendering any appreciable change in its LC properties. After cooling the liquid-crystalline samples of **1b**·TNB they were dissolved in $CDCl_3$ and subjected to ^{1}H NMR spectroscopic analysis; the resulting spectra confirmed that neither component underwent any appreciable degradation during the initial fusion and subsequent cooling process.

The excellent stability of the mesophases obtained from **1b** is potentially a very important property. However, it effectively precludes observation of the clearing transitions, thus making the resulting POM and DSC data less informative. For that reason, **1c** (which contains twice as many alkyl chains) was prepared, with the explicit expectation that it would allow for the formation of EDA-based mesophases with a narrower stability range. Samples containing **1c** and 0.5, 1.0, and 2.0 equivalents of TNB all displayed appreciable fluidity at room temperature and appeared birefringent under a polarizing microscope. Microscopy analysis of **1c**·TNB after cooling of the isotropic melt (Figure 1) shows large black homeotropic areas and "evanescent" developable cylindrical domains. Its appearance is rather untypical but can be interpreted as corresponding to a uniaxial columnar phase.[30] The texture is reminiscent of crystal spherulites (see Ref. [31]); however, closer inspection reveals the presence of dendritic patterns characteristic of a columnar phase. Finally, the texture flows under pressure and remains homogeneous, a finding that provides further support for the liquid-crystalline nature of the sample.

Differential scanning calorimetry (DSC) showed that each of the samples produced from **1c** exhibited only a single phase transition above room temperature which proved reversible upon cooling. The sample containing 1.0 equivalents of TNB gave the highest clearing point (171 °C, 4.45 $\mathrm{J\,g^{-1}}$, 18.02 $\mathrm{kJ\,mol^{-1}}$). Such a result is consistent with a **1c**·TNB adduct with a preferred stoichiometry of 1:1. Subsequent DSC cycles resulted in a depression of the clearing point, an effect that is rationalized in terms of gradual loss of TNB from the sample as a result of repeated heating (and cooling). Again, no signs of crystallization were detected by XRD when the sample was cooled, thereby indicating that the observed mesophase is thermodynamically stable.

It was subsequently found that formation of the mesophase could also be induced by exposing thin films of pure **1b** and **1c** (less than 1 µm thick) to vapors of the more volatile electron acceptors, notably trinitrotoluene (Figure 2). The induction of birefringence was observed using a polarizing optical microscope. Specifically, both the cyclopyrrole film and the TNT aliquot (ca. 0.1 µg) were incubated at 100 °C between two glass slides (Figure 2 A). Increasing the temperature accelerates the growth of the mesophase by increasing the vapor pressure of TNT and improving the fluidity of the cyclo[8]pyrrole film. The optimum film thickness, for which the strongest birefringence was observed, is approximately 0.3 µm, as estimated by optical density measurements. At this thickness the birefringent film appears yellow between crossed polarizers, and is brighter than the background (cyclo[8]pyrrole films of similar thickness that are substrate-free and hence isotropic) by about seven exposure value (EV) units. Thinner films yield weaker birefringence, which is blue to green in color. On the other hand, the observed brightness is diminished for thicker films because of the very high optical density of cyclo[8]pyrrole in the visible region.

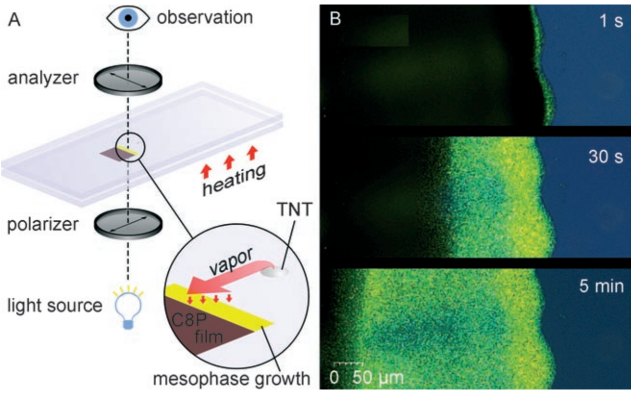

Figure 2. Formation of a cyclo[8]pyrrole-containing mesophase induced by TNT vapors. A) Experimental setup (not to scale; microscope optics omitted for clarity). B) Mesophase growth observed for **1c** at 100 °C. Left: isotropic film, dark brown; middle: mesophase, bright yellow to green, right: background, dark blue. The three photographs shown were taken approximately 1 s, 30 s, and 5 min after an aliquot of TNT (0.1 µg) was placed on the microscope slide, 1 mm from the right hand edge of the **1c** film.

The exposure of **1c** to TNT vapors has a dramatic effect on the electronic absorption spectrum of the cyclo[8]pyrrole (Supporting Information). The spectrum of a thin film of **1c** resembles the solution spectrum and features a Soret band at about 470 nm and an unusually intense and red-shifted Q band at 1100–1200 nm. Exposure of the film to TNT vapors (progress monitored by polarizing microscopy) results in the absorption spectrum showing a markedly reduced intensity accompanied by a significant change in the shape of the Q band. No such effect is observed when TNT is added to **1c** in solution. The only acceptable explanation for the hypochromism observed in the films is the existence of face-centered orbital interactions.[32] This finding is thus fully consistent with the formation of EDA-stabilized mesophases, a point that has been discussed explicitly in the context of a very different LC system reported recently by Swager, Iverson, and co-workers.[26]

More definitive evidence for the formation of the cyclo[8]pyrrole mesophases and their assignment as hexagonal columnar (Col_h) came from small-angle X-ray diffraction analyses (see Figure 1 and Table 2). The powder diffraction pattern recorded for each of the EDA-stabilized cyclo[8]-pyrrole-derived LC systems was found to exhibit two sharp small-angle X-ray reflections, with reciprocal spacings in a $1{:}\sqrt{3}$ ratio. These two features are most readily assigned as the (10) and (11) reflections from a hexagonal lattice. They are accompanied by two broad halos in the wide-angle region of the pattern: One of these invariably appears at 4.5–4.8 Å (h_{ch}) and is assigned to the molten chains with liquid-like order, while another, weaker feature, seen at 3.5–3.7 Å (h_0), corresponds to short-range face-centered contacts (namely, stacking) between the aromatic rings. In the systems containing **1b**, the h_{ch} halo is usually accompanied by another broad halo ($h_1 \approx 6.0$ Å), which is thought to correspond to the thickness of the aryl-substituted cyclopyrrole. Moreover, an additional feature at 7.2–7.3 Å (denoted h_2) was observed for **1a**·TNF which correlates well with the expected double periodicity associated with columnar stacking ($h_2 = 2h_0$). This feature is absent for systems containing TNB, TNT, and TNP. However, it may be inherently very weak in these latter cases as a result of intracolumnar disorder and short correlation lengths.[24]

Table 2: Characterization data for EDA-stabilized mesophases.

System	M [Da][a]	T [°C][a]	a [Å][a]	S [Å^2][a]	V [Å^3][a]	h [Å][a]
1a·TNF	2278.40	50	25.15	550.0	3854	7.0
1b·TNB	2800.86	200	31.15	840.0	5260	6.25
1b·TNP	2816.86	200	31.65	870.0	5290	6.0
1c·TNB	4050.98	80	33.95	1000.0	7000	7.0

[a] Explanation of symbols: M, molecular weight of the EDA adduct; T, measurement temperature; a, intercolumnar distance; S, columnar cross-section; V, molecular volume; h, intracolumnar repeat unit.

The a parameter of the lattice depends on the system studied, and was found to range from about 25 Å (**1a**·TNF) to 34 Å (**1c**·TNB). From these a values and the estimated molecular volumes V (calculated from the molar weight of the motif at a given temperature) it is possible to obtain the periodicity along the column h (Table 2). For systems containing **1a** or **1c**, the h distances are close to 7.0–7.2 Å, that is, twice the thickness of an aromatic ring (ca. 3.6 Å, here corresponding to the h_0 distance), thus leading us to suggest that the discoid adducts are not tilted. In mesophases containing **1b** the h distance is smaller and closer to the experimental h_1 distance. This difference in the h values is thought to reflect the lower chain density around the core in the case of **1b**, which may result in partial interdigitation of neighboring molecules or in a tilted arrangement of discs within the columns.

An idealized model of the Col_h mesophase, derived for **1c**·TNB, is shown in Figure 3. The van der Waals diameter of the TNB molecule is 10.2 Å, slightly less than the diameter of the macrocyclic core of the cyclo[8]pyrrole (11.7 Å). A TNB molecule can, therefore, fit within the shallow cavity created by the bulky aryl substituents of **1c**. Furthermore, once this initial interaction occurs, alternating stacks of TNB and **1c** disks can form, with each TNB ring then being encapsulated between two neighboring cyclopyrrole cores (Figure 3). These stacks may be 10 to 20 molecules long (based on the width of the h_0 feature) and are held together by EDA interactions involving the electron-rich aromatic cyclo[8]pyrrole core and the electron-deficient TNB benzene ring. Such interactions are well documented for TNB, which forms crystalline EDA complexes with molecules ranging from unsubstituted benzene[33] to predesigned supramolecular hosts.[34] While no

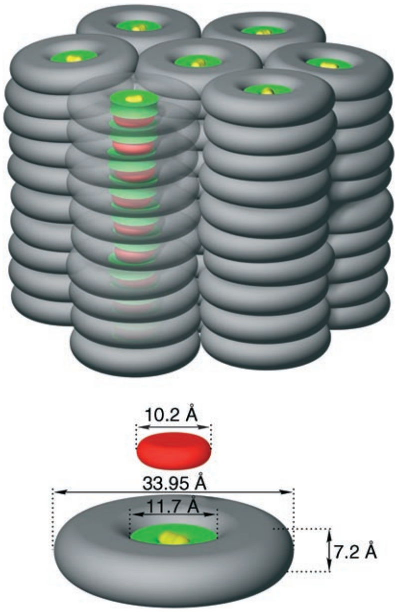

Figure 3. Idealized packing diagram for the Col_h liquid-crystalline phase of the **1c**·TNB adduct. TNB molecules (red) intercalate into stacks of cyclo[8]pyrrole cores (green; sulfate ions in yellow). The volume occupied by the substituents, including molten aliphatic chains, is shown schematically in gray. Chain interdigitatation is not shown for the sake of clarity. The diameter and thickness of the **1c** molecule were derived from the X-ray analyses reported herein, whereas the dimensions of TNB[33] and cyclo[8]pyrrole core[29] were calculated from the data reported in the literature.

solid-state data for TNB complexes with porphyrins or their analogues are as yet available, a solution study providing evidence for the formation of a 1:1 adduct between TNB and a cobalt(II) porphyrin has been reported.[22]

We believe that the self-organization of the cyclo[8]-pyrrole mesophase, which is induced by vapors of poly-nitroaromatic compounds, makes this system of potential interest in the area of explosives sensing.[35] The working principle demonstrated here, although not yet practical, could be refined to provide new sensors that could complement other recently reported materials-based approaches for the detection of explosives.[36–40] Independent of such considerations, the present EDA-based approach to stabilizing mesophases using otherwise nonmesogenic expanded porphyrin hosts may provide access to new classes of functional materials that take advantage of these unique core structures. Here, key properties include intense and extremely red-shifted electronic absorptions (above 1100 nm in the case of cyclo[8]pyrrole),[29] as well as multiple, readily available accessible oxidation states[41] that could conceivably be exploited to provide LCs with high conductivity or ones capable of supporting an enhanced generation of photocurrent.[17,18,20] Efforts to explore these various possibilities are currently ongoing.

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