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Inorganic Chemistry Article

Synthesis and Characterization of a Discotic Uranium-Containing Liquid Crystal

Jonathan L. Sessler,*,† Wyeth B. Callaway,† Stephen P. Dudek,† Richard W. Date,‡ and Duncan W. Bruce*,‡

Department of Chemistry and Biochemistry, Institute for Cellular and Molecular Biology, 1 University Station A5300, The University of Texas at Austin, Austin, Texas 78712-0165, and Department of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD, U.K.

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The synthesis of several UO_2–alaskaphyrin derivatives functionalized with aliphatic chains is described. These compounds are found to be liquid-crystalline and form columnar mesophases, as judged from polarizing optical microscopy studies, and represent the first uranium-containing discotic mesogens.

Introduction

Expanded porphyrins have attracted considerable attention of late, both for their aesthetic appeal and because of their potential utility in areas ranging from drug development to materials research.[1,2] The fact that appropriately designed systems may be used to effect anion binding, neutral substrate recognition, or cation coordination has endowed this class of molecules with considerable appeal.[3−7] Of particular interest is the ability of certain expanded porphyrins, in contrast with their more extensively studied tetrapyrrolic congeners (e.g., porphyrins, phthalocyanines), to stabilize nonlabile, in-plane, 1:1 complexes with the early actinides in the form of their high-valent oxo cations (e.g., uranyl, neptunyl, and plutonyl).[8,9] This has led us to consider that these systems could provide the basis for generating new kinds of actinide sensors as well as new classes of molecular composites. Recently, we described the synthesis of what we believe to be the first expanded porphyrin-based liquid crystals, namely metal-free systems of general structure **1**.[10] In this paper we detail the synthesis and properties of the first expanded porphyrin-based uranyl-containing metallomesogens, systems that act as thermotropic liquid crystals (cf. structure **2**; Figure 1). Although reports of uranyl-containing metallomesogens have recently appeared in the literature,[11,12] to the best of our knowledge this is the first report of a columnar mesophase derived from a uranyl species. It also appears to be the first time an expanded porphyrin-derived liquid crystal containing any kind of coordinated metal cation has been described.

Experimental Section

General Procedure. All solvents and chemicals were obtained commercially and used as received. Proton and ^{13}C NMR spectra were measured at 25 °C using a Varian Unity Innova at 300 MHz. Electronic spectra were recorded on a Beckman DU 640B spectrophotometer. High-resolution CI mass spectra were obtained on a VG ZAB2-E mass spectrometer.

The organic-solubilized 3,4-alkoxypyrroles, **7a**−**c**, were prepared as described in our recent report.[10] The requisite 1,2-diamino-5,6-

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* Authors to whom correspondence should be addressed. E-mail: sessler@mail.utexas.edu (J.L.S.), D.Bruce@exeter.ac.uk (D.W.B.). Fax: +1-512-471-7550 (J.L.S.), +44-1392263434 (D.W.B.).

† The University of Texas at Austin.

‡ University of Exeter.

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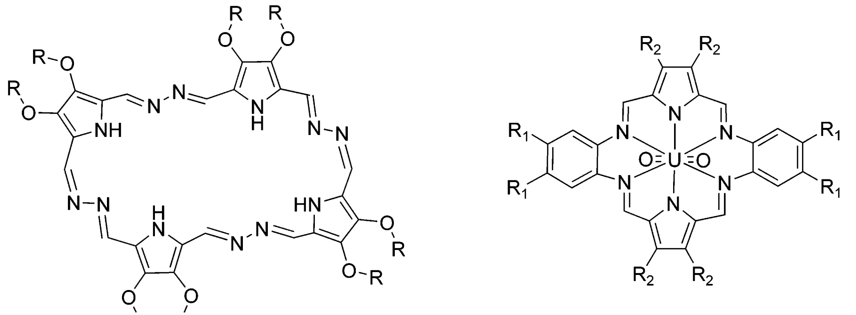

1a R = $\mathrm{CH_3}$
1b R = $\mathrm{(CH_2)_5CH_3}$
1c R = $\mathrm{(CH_2)_9CH_3}$
1d R = $\mathrm{(CH_2)_{13}CH_3}$

2a $\mathrm{R_1 = R_2 = O(CH_2)_5(CH_3)}$
2b $\mathrm{R_1 = R_2 = O(CH_2)_9(CH_3)}$
2c $\mathrm{R_1 = R_2 = O(CH_2)_{13}(CH_3)}$
2d $\mathrm{R_1 = OCH_3; R_2 = CH_2CH_3}$

Figure 1. Hyrdazinophyrin and alaskaphyrin Schiff base macrocycles. The alaskaphyrin is shown in the form of its uranyl complex.

dialkoxybenzenes, **6a**−**c**, were prepared from catechol according to the following procedures. Here, it is important to appreciate that these key intermediates proved unstable and were thus neither isolated or characterized. Rather, they were prepared in situ from the corresponding dinitro compounds, **5a**−**c**, and used immediately in the final uranyl alaskaphyrin-forming reactions.

1,2-Bis(hexyloxy)benzene (4a).[13] 1-Bromohexane (15.0 g, 90.8 mmol) was dissolved in EtOH (100 mL). KOH (6.11 g, 110 mmol) was dissolved in water (100 mL), and catechol (**3**; 5.0 g, 45.4 mmol) was added. The reaction mixture was heated under reflux for 70 h. The volatile components (presumed to be for the most part EtOH) were removed under vacuum (ca. 20 mmHg), and the residual mixture was partitioned between aqueous KOH (1 M) and ethyl acetate. The aqueous layer was extracted with ethyl acetate (3 × 150 mL). The combined organics were washed with 1 M KOH (3 × 100 mL) and brine (1 × 150 mL) to remove catechol. The organics were dried over $\mathrm{Na_2SO_4}$, and the residual solvent was removed in vacuo to yield the product in the form of a dark brown liquid (7.79 g, 62%). ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 0.90 (t, 6H, $\mathrm{OCH_2CH_2CH_2(CH_2)_2C\mathit{H}_3}$), 1.31 (m, 8H, $\mathrm{OCH_2CH_2CH_2(C\mathit{H}_2)_2CH_3}$), 1.45 (p, 4H, $\mathrm{OCH_2CH_2C\mathit{H}_2(CH_2)_2CH_3}$), 1.80 (p, 4H, $\mathrm{OCH_2C\mathit{H}_2CH_2(CH_2)_2CH_3}$), 3.98 (t, 4H, $\mathrm{OC\mathit{H}_2CH_2CH_2(CH_2)_2CH_3}$), 6.87 (s, 4H, aryl).

1,2-Bis(decyloxy)benzene (4b). This known compound[13] was prepared from 1-bromodecane in 55% yield using the procedure described above. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 0.88 (t, 6H, $\mathrm{OCH_2CH_2CH_2(CH_2)_6C\mathit{H}_3}$), 1.25 (m, 24H, $\mathrm{OCH_2CH_2CH_2(C\mathit{H}_2)_6CH_3}$), 1.39 (p, 4H, $\mathrm{OCH_2CH_2C\mathit{H}_2(CH_2)_6CH_3}$), 1.81 (p, 4H, $\mathrm{OCH_2C\mathit{H}_2CH_2(CH_2)_6CH_3}$), 3.99 (t, 4H, $\mathrm{OC\mathit{H}_2CH_2CH_2(CH_2)_6CH_3}$), 6.84 (s, 4H, aryl).

1,2-Bis(tetradecyloxy)benzene (4c). This known compound[14] was prepared from 1-bromotetradecane in 22% yield using the procedure described above. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 0.86 (t, 6H, $\mathrm{OCH_2CH_2CH_2(CH_2)_{10}C\mathit{H}_3}$), 1.24 (m, 40H, $\mathrm{OCH_2CH_2CH_2(C\mathit{H}_2)_{10}CH_3}$), 1.40 (p, 4H, $\mathrm{OCH_2CH_2C\mathit{H}_2(CH_2)_{10}CH_3}$), 1.79 (p, 4H, $\mathrm{OCH_2C\mathit{H}_2CH_2(CH_2)_{10}CH_3}$), 3.97 (t, 4H, $\mathrm{OC\mathit{H}_2CH_2CH_2(CH_2)_{10}CH_3}$), 6.86 (s, 4H, aryl).

1,2-Bis(hexyloxy)-4,5-dinitrobenzene (5a). Dialkoxycatechol **4a** (7.79 g, 28 mmol) was dissolved in acetic acid (40 mL). A mechanical stirred was attached. The solution was chilled to 0 °C, and fuming $\mathrm{HNO_3}$ (64 mL) was added. The mixture was stirred 22 h, over the course of which time a yellow solid precipitated. The mixture was poured over ice, causing more yellow precipitate to form. The solid was collected by filtration and washed with copious quantities of water to remove the acetic acid. The product was then crystallized from EtOH (125 mL) to yield the product in the form of a yellow solid (5.59 g, 33%). ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 0.89 (t, 6H, $\mathrm{OCH_2CH_2CH_2(C\mathit{H}_2)_2CH_3}$), 1.34 (m, 8H, $\mathrm{OCH_2CH_2CH_2(C\mathit{H}_2)_2CH_3}$), 1.46 (p, 4H, $\mathrm{OCH_2CH_2C\mathit{H}_2(CH_2)_2CH_3}$), 1.85 (p, 4H, $\mathrm{OCH_2C\mathit{H}_2CH_2(CH_2)_2CH_3}$), 4.08 (t, 4H, $\mathrm{OC\mathit{H}_2CH_2CH_2(CH_2)_2CH_3}$), 7.27 (s, 2H, aryl). ^{13}C NMR (500 MHz, $\mathrm{CDCl_3}$): δ 13.89, 22.47, 25.43, 28.61, 31.32, 70.16, 107.85, 136.41, 151.78. MS (CI+): *m*/*z* 369. HRMS (CI+): calcd for $\mathrm{C_{18}H_{29}N_2O_6}$, *m*/*z* 369.202 562; found, *m*/*z* 369.202 518.

1,2-Bis(decyloxy)-4,5-dinitrobenzene (5b). This compound was prepared from catechol **4b** in 25% yield using the procedure described above. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 0.86 (t, 6H, $\mathrm{OCH_2CH_2CH_2(C\mathit{H}_2)_6CH_3}$), 1.26 (m, 24H, $\mathrm{OCH_2CH_2CH_2(C\mathit{H}_2)_6CH_3}$), 1.46 (p, 4H, $\mathrm{OCH_2CH_2C\mathit{H}_2(CH_2)_6CH_3}$), 1.85 (p, 4H, $\mathrm{OCH_2C\mathit{H}_2CH_2(CH_2)_6CH_3}$), 4.08 (t, 4H, $\mathrm{OC\mathit{H}_2CH_2CH_2(CH_2)_6CH_3}$), 7.27 (s, 2H, aryl). ^{13}C NMR (500 MHz, $\mathrm{CDCl_3}$): δ 14.07, 22.65, 25.78, 28.67, 29.20, 29.29, 29.49, 29.51, 31.87, 70.18, 107.88, 136.44, 151.78. MS (CI+): *m*/*z* 481. HRMS (CI+): calcd for $\mathrm{C_{26}H_{45}N_2O_6}$, *m*/*z* 481.327 763; found, *m*/*z* 481.327 850.

1,2-Dinitro-4,5-bis(tetradecyloxy)benzene (5c). This compound was prepared from catechol **4c** in 69% yield using the procedure described above; however, stirring was maintained for 44 h. In addition the collected precipitate was dried in vacuo and was recrystallized in EtOH as reported. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 0.86 (t, 6H, $\mathrm{OCH_2CH_2CH_2(C\mathit{H}_2)_{10}CH_3}$), 1.24 (m, 40H, $\mathrm{OCH_2CH_2CH_2(C\mathit{H}_2)_{10}CH_3}$), 1.44 (p, 4H, $\mathrm{OCH_2CH_2C\mathit{H}_2(CH_2)_{10}CH_3}$), 1.85 (p, 4H, $\mathrm{OCH_2C\mathit{H}_2CH_2(CH_2)_{10}CH_3}$), 4.07 (t, 4H, $\mathrm{OC\mathit{H}_2CH_2CH_2(CH_2)_{10}CH_3}$), 7.27 (s, 2H, aryl). ^{13}C NMR (500 MHz, $\mathrm{CDCl_3}$): δ 14.10, 22.68, 25.80, 28.68, 29.22, 29.35, 29.56, 29.68, 31.91, 70.18, 107.86, 136.46, 151.77. MS (CI+): *m*/*z* 594. HRMS (CI+): calcd for $\mathrm{C_{34}H_{61}N_2O_6}$, *m*/*z* 593.452 963; found, *m*/*z* 593.452 574.

Uranyl Alaskaphyrin 2a. The 1,2-dinitrocatechol derivative prepared above (**5a**; 0.115 g, 0.37 mmol) was added to 25 mL of chilled MeOH contained in a small hydrogenator bottle. The catalyst, 10% Pd/C (0.037 mmol), was added, and the mixture was subject to hydrogenation overnight at 50 psi $\mathrm{H_2}$. The putative diamine (**6a**), presumed to be the dominant reactive organic species in the reaction mixture, was filtered through Celite directly into the reaction flask that used for the next step. The Celite and filter

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cake were washed with MeOH (ca. 10 mL), with these washing also being collected in the same reaction vessel.

To the flask containing MeOH (ca. 35 mL) and the presumed diamine (**6a**), was added the corresponding 3,4-dialkoxy-1,2-diformylpyrrole (**7a**; 0.120 g, 0.374 mmol), followed by $[UO_2(OAc)_2]\cdot 2H_2O$ (0.158 g, 0.37 mmol) and proton sponge (0.160 g, 0.74 mmol). These additions were carried out as quickly as practical to avoid any possible decomposition of the diamine. The mixture was then heated under reflux for 15 min with good stirring, during which time a dark red-brown precipitate was seen to form. The precipitate was filtered off and washed with MeOH and yielded the uranyl alaskaphyrin product **2a** in the form of a dark red-brown solid (0.169 g, 62% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 0.90 (m, $OCH_2CH_2(CH_2)_3C\mathit{H}_3$), 1.3−1.5 (m, $OCH_2CH_2(C\mathit{H}_2)_3CH_3$), 1.80 (m, $OCH_2C\mathit{H}_2(CH_2)_3CH_3$), 4.01 (t, 8H, pyrrole $OC\mathit{H}_2CH_2(CH_2)_3CH_3$), 4.15 (t, 8H, phenyl $OC\mathit{H}_2CH_2(CH_2)_3CH_3$), 6.67 (s, 4H, aryl), 8.80 (s, 4H, $C\mathit{H}{=}N$). ^{13}C NMR (500 MHz, $CDCl_3$): δ 14.01, 14.05, 22.61, 22.68, 25.71, 29.26, 29.96, 31.59, 31.65, 69.79, 74.53, 102.28, 136.71, 140.86, 141.07, 150.22, 152.05. MS (CI+): *m/z* 1459. HRMS (FAB+): calcd for $C_{72}H_{112}N_6O_{10}U$, *m/z* 1458.894 781; found, *m/z* 1458.893650. Anal. Calcd for $C_{72}H_{112}N_6O_{10}U(H_2O)_2$: C, 57.82; H, 7.82; N, 5.62. Found: C, 58.02; H, 7.60; N, 5.57.

Uranyl Alaskaphyrin 2b. This compound was prepared in 30% yield from **6b** and **7b** in accord with the above procedure. ^1H NMR (300 MHz, $CDCl_3$): δ 0.86 (m, $OCH_2CH_2(CH_2)_7C\mathit{H}_3$), 1.2−1.5 (m, $OCH_2CH_2(C\mathit{H}_2)_7CH_3$), 1.81 (m, $OCH_2C\mathit{H}_2(CH_2)_7CH_3$), 4.01 (t, 8H, Pyrrole $OC\mathit{H}_2CH_2(CH_2)_7CH_3$), 4.15 (t, 8H, Phenyl $OC\mathit{H}_2CH_2(CH_2)_7CH_3$), 6.66 (s, 4H, Aryl), 8.80 (s, 4H, $C\mathit{H}{=}N$). ^{13}C NMR (500 MHz, $CDCl_3$): δ 14.08, 22.68, 26.05, 26.07, 29.32, 29.35, 29.36, 29.46, 29.51, 29.60, 29.62, 29.65, 29.70, 30.02, 31.91, 31.92, 69.76, 74.48, 102.27, 136.64, 140.80, 141.05, 150.18, 152.08. ESI (CI+): *m/z* 1909. HRMS (FAB+): calcd for $C_{104}H_{176}N_6O_{10}U$, *m/z* 1907.395 583; found, *m/z* 1907.389 394. Anal. Calcd for $C_{104}H_{176}N_6O_{10}U(H_2O)_2$: C, 64.23; H, 9.33; N, 4.32. Found: C, 64.37; H, 9.33; N, 4.34.

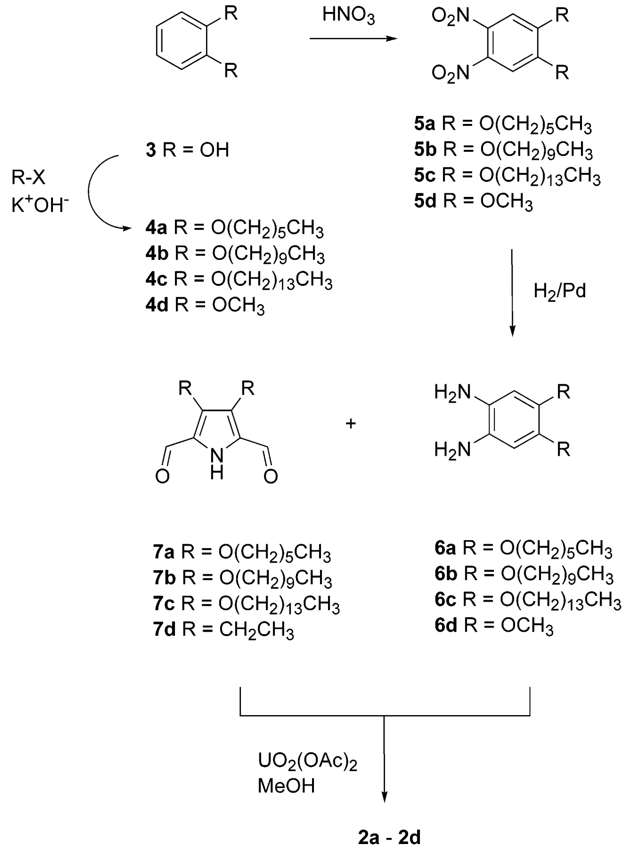
Uranyl Alaskaphyrin 2c. This compound was prepared in 20% yield from **6c** and **7c** in accord with the above procedure. ^1H NMR (300 MHz, $CDCl_3$): δ 0.91 (m, $OCH_2CH_2(CH_2)_{11}C\mathit{H}_3$), 1.0−1.6 (m, $OCH_2CH_2(C\mathit{H}_2)_{11}CH_3$), 1.85 (m, $OCH_2C\mathit{H}_2(CH_2)_{11}CH_3$), 4.05 (t, 8H, Pyrrole $OC\mathit{H}_2CH_2(CH_2)_{11}CH_3$), 4.21 (t, 8H, Phenyl $OC\mathit{H}_2CH_2(CH_2)_{11}CH_3$), 6.71 (s, 4H, Aryl), 8.85 (s, 4H, $C\mathit{H}{=}N$). ^{13}C NMR (500 MHz, $CDCl_3$): δ 14.10, 22.69, 26.07, 26.09, 29.37, 29.48, 29.52, 29.68, 29.73 (broad), 30.03, 31.93, 69.81, 74.54, 102.32, 136.70, 140.85, 141.08, 150.23, 152.06. HRMS (FAB+): calcd for $C_{136}H_{240}N_6O_{10}U$, *m/z* 2355.896 386; found, *m/z* 2355.887 596. Anal. Calcd for $C_{136}H_{240}N_6O_{10}U(H_2O)_{3.5}$: C, 67.48; H, 10.29; N, 3.47. Found: C, 67.46; H, 9.99; N, 3.69.

Phase Studies. Studies by optical microscopy were carried out as described previously.[15]

Results and Discussion

Systems **2a**−**c** were targeted for synthesis as they are based on the well-known alaskaphyrin core and because the presence of eight peripheral chains was likely to promote the necessary structural anisotropy to allow for liquid-crystal phase formation. The alaskaphyrin expanded porphyrin (3,10,17,24,29,30-hexaazapentacyclo-$[24.2.1.1.^{12,15}0.^{4,9}0.^{4,9}0^{18,23}]$triaconta-2,4,6,8,10,12,14,16,18,-20,22,24,26,28-tetradecaene) forms a very stable 1:1 complex with the uranyl cation (cf. Figure 1) and, indeed, is most easily prepared from its diformylpyrrolic and *ortho*-phenylenediamine constituents via a uranyl-templated condensation process (to give, e.g., **2d**). It was thus thought that if *ortho*-phenylenediamines could be prepared, suitably substituted by alkyl chains, then condensation with our recently reported 3,4-dialkoxy-2,5-diformylpyrroles (**7a**−**c**)[10] in the presence of the uranyl cation would yield the desired actinide-cation-containing mesogens in one simple step. This direct approach is advantageous in that the separation and purification procedures are more straightforward.

Scheme 1



Scheme 1 summarizes the chemistry used to produce alaskaphyrins **2a**−**c**. Briefly, catechol (**3**) was reacted with a long-chain alkyl halide to give the corresponding dialkoxy species. Nitration with fuming nitric acid then gave rise to the intermediate dialkylated dinitro catechol derivatives **5a**−**c**. In situ reduction produced the presumed diamines, **6a**−**c**. These latter compounds proved unstable, and therefore, reduction of **5a**−**c** was followed by an almost immediate condensation with the appropriate 3,4-dialkylated-2,5-diformylated pyrroles, **7a**−**c**, in the presence of excess uranyl acetate. In accord with what had been observed previously in the case of the reaction of **6d** and **7d**,[16] this produced the desired alaskaphyrin derivatives **2a**−**c** in low to moderate yield. These species displayed spectral data in accord with their expected structures and were thus taken on for testing as potential liquid-crystalline materials.

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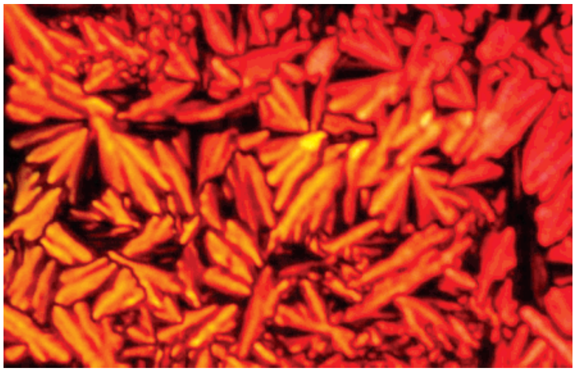

Figure 2. Uranyl complex of **2b** forming a liquid crystal, as seen through photomicrography. The mesophase is observed here at 124 °C and is stable between 108 and 135 °C.

The liquid-crystalline properties of **2a**−**c** were probed by polarized optical microscopy. The results obtained confirmed that two out of three of the compounds, namely **2b**,**c**, were mesomorphic, while **2a** simply melted directly to the isotropic phase at 110 °C. On examination of **2b**,**c**, both appeared as soft solids at room temperature and melted to a mesophase on heating to 108 and 106 °C, clearing at 133 and 135 °C, respectively. On cooling, the mesophase appeared just a few degrees below the clearing point and the texture was rather fine, unlike that which we observed with the recently reported hydrazinoporphyrin,[10] which may well be due to the higher viscosity found in the present materials. The texture is illustrated in Figure 2. Identification of the mesophase on the basis of the optical texture is not unequivocal, but the presence of homeotropic domains in some preparations would suggest strongly that the phase is columnar hexagonal. On cooling, the compounds did not crystallize but appeared to form a glass.

To compare these results with a metal-free analogue of alaskaphyrin, the appropriate starting materials were condensed with an acid catalyst in the absence of the templating metal. These conditions, however, did not result in formation of the macrocycle. Attempts were then also made to demetalate compounds, **2a**−**c**, using a variety of conditions; however, all those tested resulted in either decomposition of the macrocycle or return of the starting material. Thus, in contrast to what proved true for **2d**, as yet, we have been unable to prepare the metal-free form. Thus, even though the uranyl center is apparently required to stabilize these particular alaskaphryins, this same requirement has made it impossible to judge the effects of the cation on the liquid-crystalline properties. Current work is, therefore, focused on systems that allow the construction of both metalated and unmetalated, actinide-coordinating liquid crystals. Such systems could have an important role as, e.g., specific cation sensors.

Conclusion

The present paper describes the first time an actinide has been incorporated into a discotic liquid crystal and the first time a metal-containing expanded porphyrin-based liquid-crystalline material has been prepared. It thus serves to support the emerging notion that expanded porphyrins may have a role to play in the construction of novel liquid-crystalline phases. The combined features of planarity and intermolecular π-stacking are key attributes[17] that are thought to favor the formation of columnar mesophases. The fact that certain expanded porphyrins, like the alaskaphyrins of this report, have the ability to coordinate actinides, while others can act as receptors for neutral or anionic substrates, makes them attractive as potentially environmental-sensitive sensors since the resulting changes (from, e.g liquid-crystalline to non-liquid-crystalline as a function of external stimuli) would serve to signal the presence of the targeted analyte in a particularly dramatic way. Current efforts are thus devoted to preparing such systems as well as to studying the effects that coordination within an alaskaphyrin core has on the intrinsic properties of a bound actinide cation.

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(17) However, these features are not a requirement for the formation of columnar mesophases. There are known examples in the literature of columnar mesophase forming materials that are neither planar nor capable of π-stacking. See e.g.: Blake, A. J.; Bruce, D. W.; Fallis, I. A.; Parsons, S.; Richtzenhain, H.; Ross, S. A.; Schröder, M. *Proc. R. Soc. London A* **1996**, *354*, 395−414.