Enantioseparation of Racemic Organic Molecules by a Zeolite Analogue[**]

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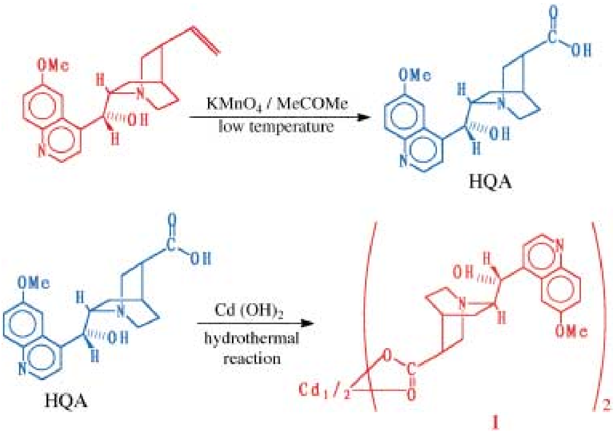
The rational design and construction of hybrid organic–inorganic zeolite analogues (HOIZAs) for enantioseparation and catalysis is of intense current interest. These solids have shown their potential to control the host–guest chemistry of the framework by tailoring or tuning the chemical building blocks from which the network is assembled.[1–6] Through the incorporation of appropriate organic ligands the polarity of an intraframework void may be tuned to attract a range of guest molecules. This potential is not available with pure inorganic zeolites.[1] The inclusion of enantiomerically pure chiral building blocks into microporous materials (zeotypes) for enantiomer separation, as well as chiral synthesis and catalysis, has been a continuing challenge and represents an ambitious goal for chemists.[2–4]

Currently known materials capable of offering enantiomeric separation and catalysis tend to be 2D layer-type structures that are able to intercalate guests.[1, 5] Attempts to resolve enantiomers using zeolite beta, one polymorph of which crystallizes in the chiral space group $P4_122$, have as yet been unsuccessful.[6] It is known that some 3D metal coordination polymers, such as chiral coordination polymers, can reversibly exchange guest molecules while maintaining crystallinity.[7–22] These materials, however, are constructed from achiral building blocks. As a consequence, the product is a racemic mix of crystals, although their single crystals are enantiomeric. Enantiomerically pure HOIZAs with intraframework voids capable of accommodating guest molecules are highly desirable. Ideally, such a 3D framework should have relatively high thermal stability and rigidity, and possess channels that permit reversible inclusion of guests. To the best of our knowledge the existence of chiral 3D HOIZAs capable of resolving racemic guest molecules by the reversible inclusion/removal of guests is unknown. Here we report a robust 3D enantiopure HOIZA capable of resolving racemic mixtures of small organic molecules.

Our strategies employed in preparing such a material involve the rational design and use of functionalized chiral ligands that are capable of bridging metal centers to form an open framework. Specifically, such a framework is produced in a self-assembly process by linking cationic metal centers and an enantiopure chiral bridging ligand containing the following functional groups:

1. A carboxylate binding group that makes the ligand anionic and the framework neutral. This ensures that intraframework voids are not occupied by counterions.
2. A mix of hydrophobic and hydrophilic groups that induce the inclusion of a variety of guests.
3. A pyridyl-type group that is able to satisfactorily complete the coordination sphere of the metal center in the generation of a 3D diamondoid coordination polymer.[23–27]

One candidate that fulfils these requirements is quitenine (6′-methoxyl-(8*S*,9*R*)-cinchonan-9-ol-3-carboxylic acid (HQA)). The enantiopure chiral building block HQA, which is prepared from the off-the-shelf antimalarial alkaloid quinine,[28] reacts with $Cd(OH)_2$ to give HOIZA $[Cd(QA)_2]$ (**1**, Scheme 1) with a homochiral open channel 3D structure.[29] The crystal structure of **1** (Figure 1) shows each Cd^{2+} ion is in a



Scheme 1. Synthesis of quitenine (HQA) and the cadmium complex **1**.

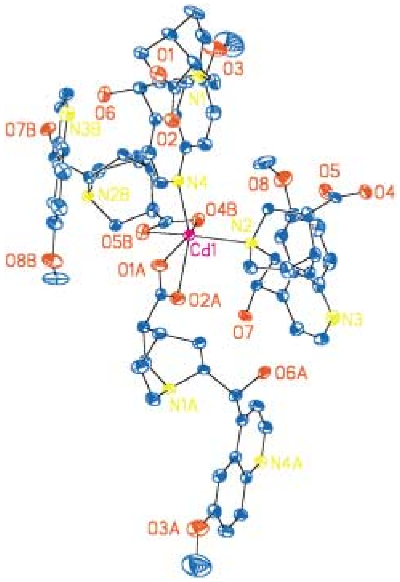


Figure 1. ORTEP view of an asymmetric unit of **1** (30 % probability displacement ellipsoids). The H atoms are omitted for clarity.

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[**] This work was supported by The Major State Basic Research Development Program (Grant No. G2000077500), the National Natural Science Foundation of China, the Camille Dreyfus Teacher–Scholar Program, the National Science Foundation of the USA (CHE-9904338), and the University of Tennessee SARIF EPPE Fund.

1433-7851/01/4023-4422 $ 17.50+.50/0

distorted octahedral geometry and coordinated by two nitrogen atoms and the oxygen atoms of two carboxylate groups. There are two clearly distinct QA$^-$ ligands in **1**. Although both ligands bridge Cd^{2+} centers, they differ significantly in their mode of binding. In both cases the carboxylate groups chelate the metal center but in only one case is the quinoline unit binding to a neighboring Cd^{2+} center. In the other ligand the alipahtic amine coordinates to an adjacent Cd^{2+} ion while the quinoline moiety is uncoordinated. Thus, each Cd^{2+} ion is coordinated by four ligands that bridge to four other symmetry-related Cd^{2+} ions. The Cd^{2+} ions linked by the QA$^-$ ligands that bind through the quinoline group are 10.7 Å apart, while the Cd^{2+} centers bridged by the ligands involving coordination of the aliphatic amine are 7.8 Å apart.

From a topological perspective, each Cd^{2+} ion acts as a four-connecting center in a 3D network. The connectivity of this network (Figure 2) is the same as that found in diamond, although it is somewhat distorted from the ideal cubic structure. As indicated above, the connections between the four-connecting Cd^{2+} centers are not all of the same length and the Cd-Cd-Cd angles fall in the range 98–152°, as compared to the ideal tetrahedral angle of 109.5° found for the C-C-C angles in diamond.

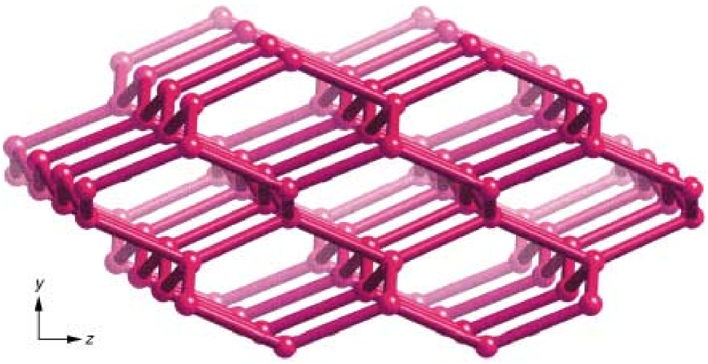
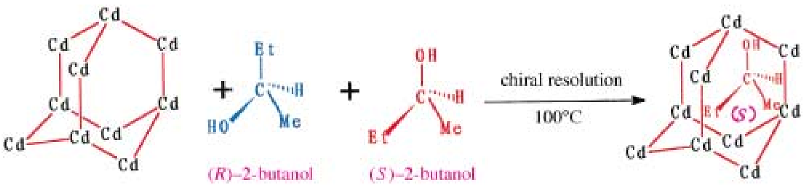


Figure 2. A topological perspective view of **1** in which the straight lines and circles represent the quitenine ligands and Cd atoms, respectively.

Many coordination networks with open framework structures are interpenetrated by independent networks that fill the intraframework voids. No interpenetration is, however, observed in this structure. The absence of interpenetration results in a lattice with maximum space available for the guest.

Thermogravimetric analysis (TGA) was performed on a polycrystalline sample of **1** to gauge its thermal stability. No clean weight-loss step occurred below 265 °C, which indicates that the network structure is stable below that temperature.

The chirality of the framework suggests that the intraframework voids may provide a chiral environment for guest molecules. Within a diamond network the voids may be considered to lie within adamantane-type cavities (Scheme 2). This asymmetric structural feature in **1** has the potential to allow enantioselective separation of small organic molecules, such as racemic 2-butanol and 2-methyl-1-butanol.



Scheme 2. Inclusion of (*S*)-2-butanol in the adamantane-like cavities of **1**.

In order to investigate whether this coordination polymer allows enantioselective separation, racemic 2-butanol and a powdered sample of [Cd(QA)$_2$] (**1**) were mixed under solvothermal reaction conditions. A crystalline sample of ((*S*)-2-butanol) $\subset$ [Cd(QA)$_2$] (**2**) was obtained. A single-crystal X-ray structural determination[30] clearly shows that (*S*)-2-butanol has been included in **2** (Figure 3). Examination of the 2-butanol desorbed from **2** showed that it had a specific optical rotation ($[\alpha]_D^{20} = +13.0°$ (neat)) identical to that of a pure (*S*)-2-butanol standard. The *ee* value was estimated to be approximately 98.2 %. The adamantane-type cavity within the structure is represented in Figure 4, and it clearly shows the (*S*)-2-butanol lies within the chiral cavity of this network. A TGA of powdered polycrystalline (*S*)-2-butanol $\subset$ [Cd(QA)$_2$] indicated that a weight loss of approximately 8.3 % in the 160–204 °C range corresponds to the complete removal of all the (*S*)-2-butanol (calculated 8.51 %). The framework is thermally stable up to about 265 °C. This coordination polymer (**2**) is, to our knowledge, the first HOIZA that exhibits enantioselective reversible inclusion of a molecular guest without change to the framework structure. In addition its ability to resolve organic enantiomers is unprecedented.

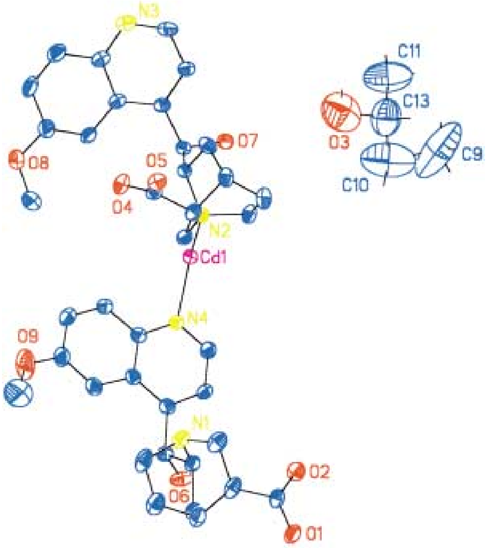


Figure 3. ORTEP view of an asymmetric unit of **2** (30 % probability displacement ellipsoids). The H atoms of the frameworks are omitted for clarity.

(*S*)-2-methyl-1-butanol $\subset$ [Cd(QA)$_2$] (**3**), an analogue of **2** with a larger chiral organic guest, was also prepared from racemic 2-methyl-1-butanol by a procedure similar to that

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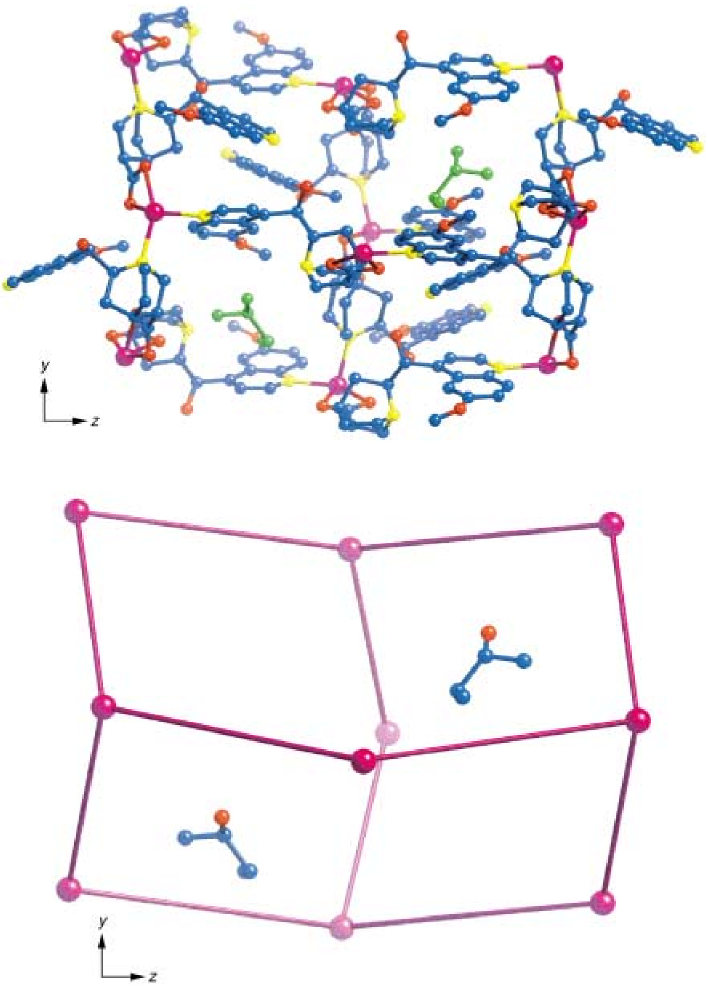

Figure 4. Top: Part of the diamond-like network of **2** including (*S*)-2-butanol. Bottom: A simplified diamond-like network clearly showing the (*S*)-2-butanol sites in the chiral cavity.

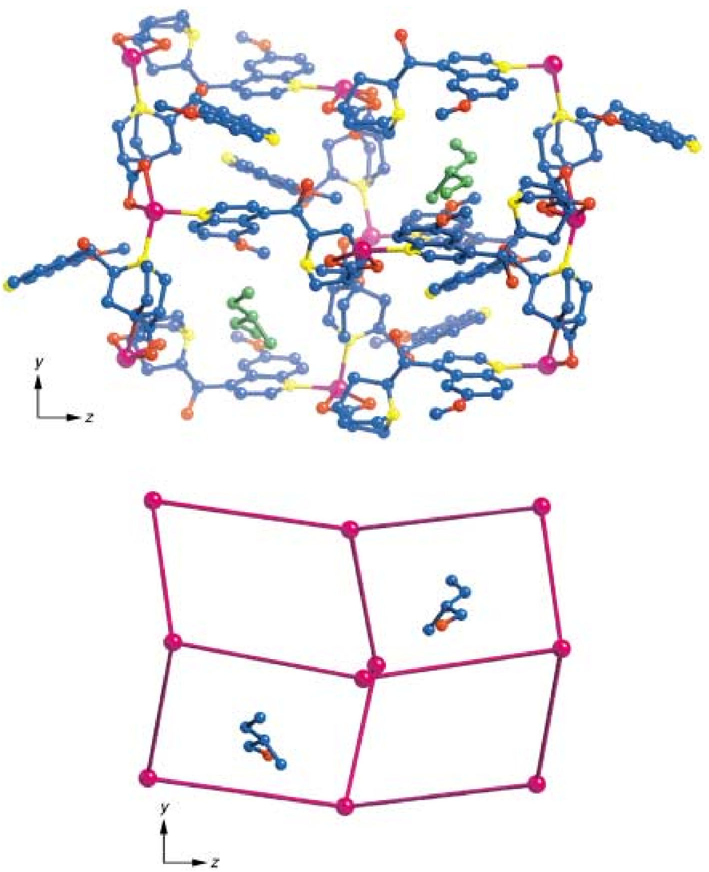

Figure 6. Top: Part of the diamond-like network of **3** including (*S*)-2-methyl-1-butanol. Bottom: A simplified diamond-like network clearly showing the (*S*)-2-methyl-1-butanol sites in the chiral cavity.

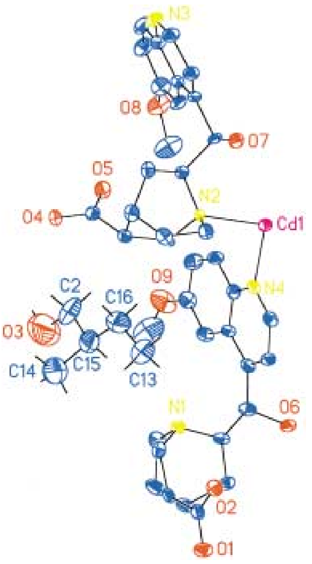

Figure 5. ORTEP view of an asymmetric unit of **3** (30% probability displacement ellipsoids). The H atoms of the frameworks are omitted for clarity.

used in the synthesis of **2**.[31] The solid-state structure (Figure 5) shows that **3** is isostructural with **2**, and that the 2-methyl-1-butanol included is the *S* enantiomer. Similarly, the adamantane-type cavity within the structure is represented in Figure 6, and it clearly shows the (*S*)-2-methyl-1-butanol molecule lies within the chiral cavity of this network. The optical rotation ($[\alpha]_D^{23} = -5.8°$ (neat)) of the 2-methyl-1-butanol desorbed from **3** is identical to the standard (*S*)-2-methyl-1-butanol with an *ee* value of about 8.4%. TGA indicates that **3** begins to lose (*S*)-2-methyl-1-butanol at 80 °C and that the $[Cd(QA)_2]$ framework is stable up to about 265 °C. Further investigations on the resolution of other small molecules are currently underway.

Experimental Section

HQA: Slow oxidation of quinine (6.5 g, 20 mmol) with $KMnO_4$ (9.5 g, 60 mmol) in aqueous acetone at 0–5 °C afforded a colorless prismatic crystalline product, which after recrystallization from water and ethanol gave 2.49 g (6.0 mmol, 30% yield) of quitenine · $4H_2O$. Elemental analysis calcd for $C_{19}H_{23}N_2O_4 \cdot 4H_2O$: C 55.06, H 7.30, N 6.76%; found: C 55.11, H 7.31, N 6.81; IR (KBr): $\tilde{\nu} = 3395$(br, s), 2952(w), 1621(s), 1591(s), 1509 (m), 1473(m), 1435(w), 1369(m), 1242(m), 1025(w), 856(w), 834(w), 718(w), 640(m) cm^{-1}.

1: Hydrothermal treatment of $Cd(OH)_2$ (0.293 g, 2 mmol) and quitenine (1.657 g, 4 mmol) in ethanol for three days at 100 °C afforded 0.954 g (1.2 mmol, 60% yield) of **1** as colorless crystals. Elemental analysis calcd for $C_{38}H_{42}N_4O_8Cd$: C 57.35, H 5.28, N 7.04%; found: C 57.41, H 5.31, N 6.91; IR (KBr): $\tilde{\nu} = 3396$(br, s), 2945(m), 1623(s), 1543(s), 1513(s), 1474(s), 1410(s), 1244(m), 1228(m), 1103(w), 1029(w), 949(w), 854(w), 832(w), 781(w), 718(w), 642(w), 607(w) cm^{-1}.

2: Hydrothermal reaction of **1** (1.590 g, 2 mmol) with a solution of racemic 2-butanol for three days at 100 °C afforded 0.956 g (1.10 mmol, 55% yield) of **2** as colorless crystalline plates. Elemental analysis calcd for $C_{42}H_{52}N_4O_9Cd$: C 57.98, H 5.98, N 6.44%; found: C 58.04, H 5.86, N 6.51; IR (KBr): $\tilde{\nu} = 3416$(br, s), 2943(m), 1622(s), 1552(s), 1513(s), 1412(s), 1278(w), 1243(w), 11228(w), 1104(w), 1030(m), 856(w), 833(w), 717(w), 642(w), 606(w) cm^{-1}.

3: Hydrothermal reaction of **1** (1.590 g, 2 mmol) with a solution of racemic 2-methyl-1-butanol for three days at 100 °C afforded 1.324 g (1.5 mmol, 75% yield) of **3** as colorless crystalline plates. Elemental analysis calcd for $C_{43}H_{54}N_4O_9Cd$: C 58.42, H 6.11, N 6.34%; found: C 58.42, H 6.19, N 6.41;

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}.

Received: July 16, 2001 [Z17516]

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[28] Crystal data for quitenine · 4 H$_2$O: $C_{19}H_{30}N_2O_8$, orthorhombic, space group $P2_12_12_1$, $a = 9.5585(9)$, $b = 10.3410(9)$, $c = 20.8404(19)$ Å, $\alpha = \beta = \gamma = 90.00°$, $V = 2060.0(3)$ Å^3, $Z = 4$, $M_r = 414.45$, $\rho_{calcd} = 1.336$ Mg m^{-3}, $R_1 = 0.0667$, $wR_2 = 0.1770$, $T = 293$ K, $\mu = 1.040$ mm^{-1}, $S = 1.265$, Flack $\chi = 0.001(2)$.

[29] Crystal data for **1**: $C_{38}H_{42}N_4O_8Cd$, orthorhombic, space group $P2_12_12_1$, $a = 13.8639(8)$, $b = 15.1012(8)$, $c = 19.4313(11)$ Å, $\alpha = \beta = \gamma = 90.00°$, $V = 4068.0(2)$ Å^3, $Z = 4$, $M_r = 795.16$, $\rho_{calcd} = 1.298$ Mg m^{-3}, $R_1 = 0.0646$, $wR_2 = 0.1358$, $T = 293$ K, $\mu = 0.588$ mm^{-1}, $S = 1.017$, Flack $\chi = 0.01(3)$.

[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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[**] We thank P. Zell for his assistance in the practical work, Frau G. Dörfner and Prof. U. Thewalt (Sektion Röntgenbeugung, Universität Ulm) and Dr. B. Heise (Abteilung Experimentelle Physik, Universität Ulm) for X-ray diffraction studies. Financial support from the Deutsche Forschungsgemeinschaft (Habilitandenstipendium for F.W.), the Fonds der Chemischen Industrie (Liebig-Stipendium for F.W.), and the Dr. Otto Röhm Gedächtnisstiftung is gratefully acknowledged.

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