Liquid Crystals

International Edition: DOI: 10.1002/anie.201505278
German Edition: DOI: 10.1002/ange.201505278

Liquid-Crystalline Mesogens Based on Cyclo[6]aramides: Distinctive Phase Transitions in Response to Macrocyclic Host–Guest Interactions

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Abstract: *Producing macrocyclic mesogens that are responsive to guest encapsulation presents a significant challenge. Cyclo[6]aramides, a type of macrocycle with a hydrogen-bond-constrained backbone, exhibit thermotropic lamellar, discotic nematic, hexagonal, and rectangular columnar mesophases over a considerably wide temperature range, including at room temperature. Additionally, cyclo[6]aramides show unusual mesophase transitions from lamellar to hexagonal columnar phase mediated by macrocyclic host–guest (H–G) interactions between the macrocycles and alkylammonium salts. The phase transition, triggered by an organic guest engaging in H–G interactions with a macrocyclic cavity, provides a novel strategy for manipulating the properties of liquid-crystalline materials. The crystal structure of a homologous cyclo[6]aramide reveals a disk-shaped, near-planar molecular backbone that facilitates intermolecular π–π stacking and leads to columnar assembly.*

Uncovering new macrocyclic mesogens often leads to the discovery of functional materials endowed with unique liquid-crystal behavior.[1] Early work on macrocyclic mesogens included reports on conformationally flexible mesogens composed of macrocyclic oligoethers or paracyclophane.[2] Among macrocycles that could serve as the constituents of mesophases, those with a more or less rigid core bearing peripheral flexible side groups are recognized as successful discotic liquid-crystalline (LC) materials, as typically demonstrated by phenylacetylene macrocycles,[3] Schiff-base macrocycles,[4] porphyrins,[5] phthalocyanines,[6] cyclopeptides,[7] cyclo[8]pyrroles,[8] pillar[5]arenes,[9] calixarenes,[10] and other cyclic species.[11] In many cases, the observations of LC properties rely heavily on the presence of an additional mesogenic handler.[7,9,12] Furthermore, producing macrocyclic mesogens with rich mesomorphic phases over wide temperature ranges is still a formidable task. Recently, host–guest (H–G) interactions involving macrocyclic molecules have been intensely investigated to construct various supramolecular architectures.[13] Surprisingly, despite their inner cavities, none of the currently known macrocycles have been explored to effect the phase transition of LC materials by taking advantage of H–G interactions. We report herein that, with appropriate peripheral structural modifications, cyclo[6]aramides **1a**–**1e** (Figure 1), derived from hydrogen-bonded (H-bonded) aromatic amide foldamer precursors,[14] could serve as a new class of mesogens to form rich mesophases. These mesophases, including thermotropic lamellar, discotic nematic, hexagonal, and rectangular columnar mesophases, form over a very wide temperature range including at room temperature. This constitutes the first observation of tunable LC phases of mesogens based on a highly effective shape-persistent macrocyclic backbone. More importantly and significantly, in the case of **1c** a distinct phase transition from a lamellar to a hexagonal mesophase could be induced through macrocyclic H–G interactions upon the addition of cationic guests, such as triethylammonium chloride, which offers a new strategy for tuning mesophase

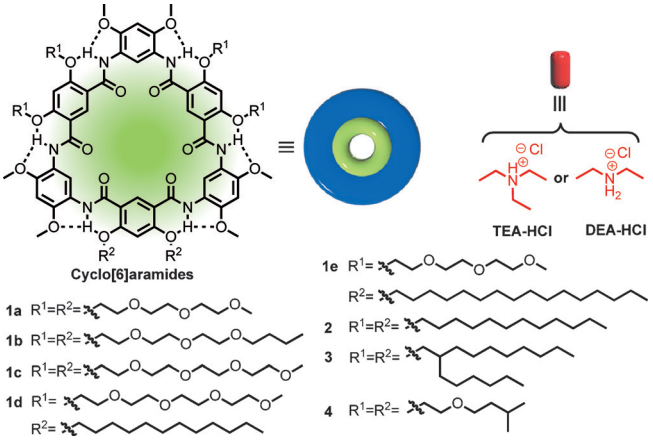

Figure 1. Molecular structures and schematic representation of cyclo[6]aramides **1**–**4** and alkylammonium chlorides.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201505278.

transitions. A single crystal of macrocycle **4**[15] was obtained to help elucidate a possible self-assembly mechanism to explain the occurrence of liquid crystallinity.

In recent years, H-bonded aromatic amide macrocycles,[16] featuring amide linkages and a persistent molecular shape, have received increasing attention because of their interesting H–G chemistry and the ability to form channels through self-assembly.[16c,17] In particular, macrocycles with amide oxygen atoms inwardly oriented are intriguing in their ability to form H–G complexes. Nevertheless, mesomorphism for these macrocycles has never been reported since their discovery a decade ago.[18] Given the backbone conformation of these macrocycles, that is, with a near-planar disc-shaped large π surface,[19] we speculate that the smallest member of the macrocycle family, denoted cyclo[6]aramide,[20] may exhibit interesting mesophases.

Results based on acyclic analogues of cyclo[6]aramides show that a balanced core dimension and flexible periphery could impart the designed oligoamide with mesomorphism.[21] Unexpectedly, compounds **2** and **3** with alkyl side chains failed to show any LC properties. This prompted us to prepare a series of compounds **1a**–**1e** bearing oligoether side chains or a combination of polar and alkyl chains attached to the periphery of the macrocycle.[3f,4b] The resultant macrocycles were unambiguously characterized by NMR and MALDI-TOF mass-spectral analyses (see Figures S1–13 in the Supporting Information). Thermogravimetric analysis of **1**–**3** revealed no mass loss up to circa 300 °C, indicating the great thermal stability of these macrocycles (Figure S14–21, Table S1). Furthermore, intramolecular H-bonding was found to remain essentially unchanged as inferred from the lack of an N–H stretching frequency shift around 3380 cm^{-1} in variable-temperature FTIR spectra (Figure S22–26). These results suggest the persistence of a macrocyclic backbone at high temperatures.

Indeed, replacing all the alkyl chains of **2** with polar triethylene glycol (TEG) chains led to compound **1a**. This compound exhibits a dendritic texture in polarized optical microscopy (POM) images over a temperature range from 170 °C to 66 °C that is characteristic of classical textures of hexagonal columnar phases (Col_h; Figure 2a,g). A phase-transition behavior for **1a** was identified by differential scanning calorimetry (DSC) analysis (Figure S34). Consistent with the microscopic data, variable-temperature X-ray diffractions showed patterns characteristic of a Col_h phase (Figure S44,45). Typically, the XRD pattern at 160 °C (Figure 3a) for the oriented sample reveal five reflections at 23.25, 13.51, 11.78, 8.84, and 7.76 Å in the low-angle regime with the reciprocal spacing ratio of 1: $1/\sqrt{3}$: 1/2: $1/\sqrt{7}$: $1/\sqrt{9}$. They are assigned as the (100), (110), (200), (210), and (300) reflections, respectively, which are indicative of a hexagonal phase with a periodicity of 26.85 Å (Table S6). Additionally, the d spacing of 3.88 Å agrees well with typical aromatic π–π stacking distance.

Elongation of peripheral groups afforded macrocycles **1b** and **1c**. As expected, both compounds also exhibit columnar liquid crystallinity (Figure 2b,c, and g). However, they both show enhanced clearing temperatures over 225 °C (the temperature over which the compound exists as an isotropic liquid) on the second heating, suggesting the significant influence of polarity and side-chain length on the LC properties. In contrast to **1b**, the DSC trace of **1c** shows two enantiotropic phase transitions at 68.95 and 225.41 °C with a wide temperature range of 156.46 °C. Interestingly, the POM images of **1c** reveal spherical textures with a black cross in the center from the isotropic temperature up to 190 °C in the first cooling. However, the texture disappears at 190 °C into a mosaic texture. This clearly indicates the presence of two different mesophases for **1c**, which is corroborated by variable-temperature XRD experiments (Figure S50). The XRD pattern at 180 °C in the low-angle regime reveals diffraction peaks with the reciprocal spacing ratio of 1:1/2:1/3:1/4:1/5, confirming the presence of a layered phase with a periodicity of 23.21 Å. In contrast, the XRD pattern at

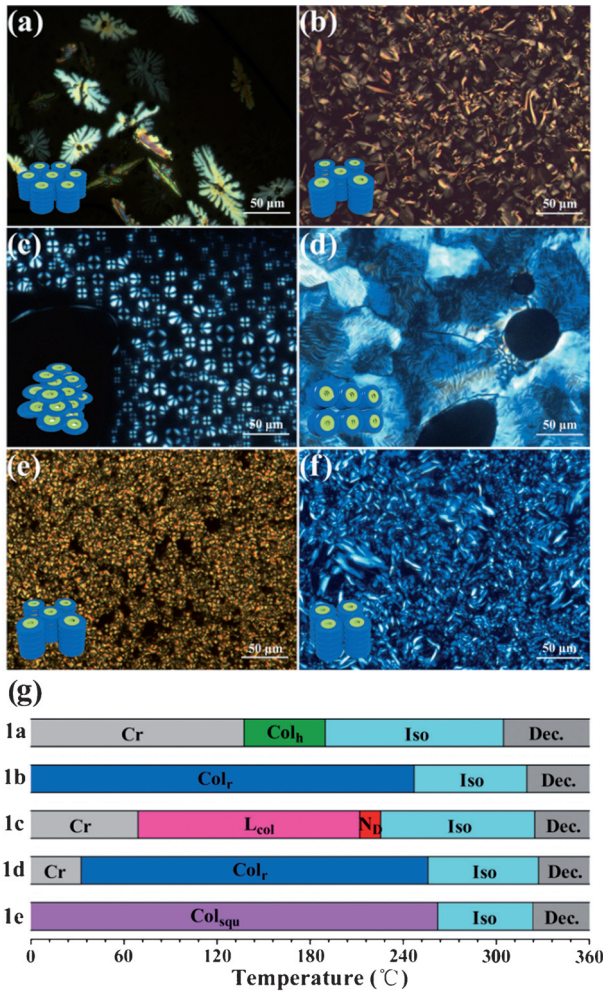

Figure 2. Polarized optical micrograph of a) Col_h of **1a** at 120 °C, b) Col_r of **1b** at 217 °C, c) N_D of **1c** at 210 °C, d) L_{col} of **1c** at 100 °C, e) Col_{squ} of **1d** at 200 °C, and f) rectangular columnar mesophase of **1e** at 100 °C upon cooling from the isotropic melt. Scale bar in (a–f) = 50 μm. g) Phase diagrams of the macrocycles **1a**–**1e** traced during the second heating cycle in DSC with a heating rate of 10 °C min^{-1}. Phase notations: Cr = crystal; Col_h = hexagonal columnar mesophase; Col_r = rectangular columnar mesophase; L_{col} = columnar lamellar mesophase; N_D = discotic nematic mesophase; Col_{squ} = tetragonal columnar mesophase; Iso = isotropic liquid.

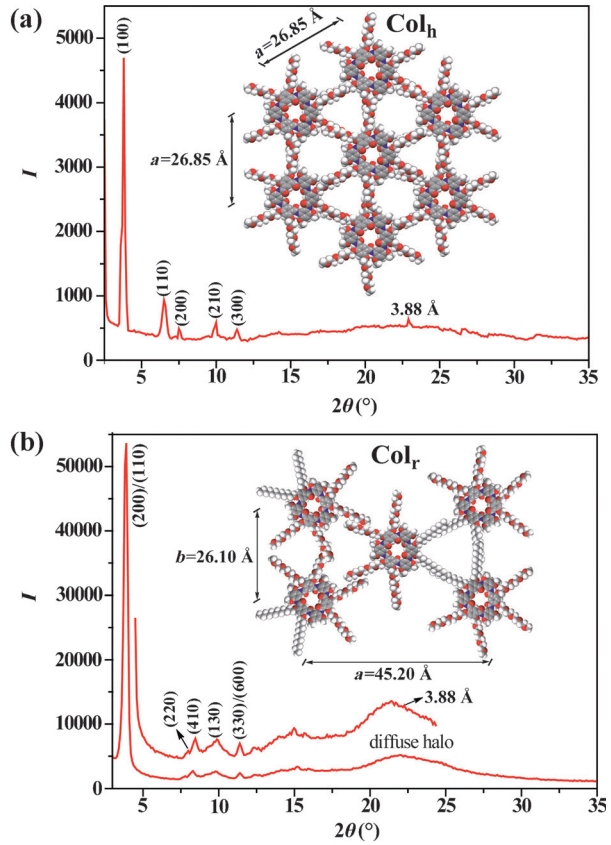

Figure 3. X-ray diffraction patterns of a) **1a** at 160 °C and b) **1d** at 230 °C on cooling from the isotropic phase at a cooling rate 2 °C min^{-1}. Inset in (a) and (b): possible 2D packing models for a) **1a** in its hexagonal columnar mesophase at 160 °C and b) **1d** in its rectangular columnar mesophase at 230 °C.

200 °C shows no obvious reflection peaks in the low-angle regime. This observation is significant as it is extremely rare for a cavity-containing macrocycle to display such a distinct mesophase transition.[4b]

Given that peripheral substitution with linear alkyl chains greatly promotes the intermolecular aggregation that is necessary for columnar stacking[22] and that the introduction of polar ether chains tends to result in mesomorphism,[4b,21c] the amalgamation of both traits is expected to provide an alternative means to fine-tune LC properties. This led to the design of amphiphilic cyclo[6]aramides **1d** and **1e**. Indeed, both compounds exhibit columnar liquid crystallinity (Figure 2d, e, and g) with rectangular (Figure 3b) and square phases. The higher clearing points and the much wider temperature ranges (> 220 °C) for **1d** and **1e**, compared with **1a**–**1c**, are especially noteworthy. This is most likely because of the enhanced π–π stacking interaction associated with a nanoscale phase separation caused by the two types of incompatible side chains of **1d** and **1e**.[5b] It should be noted that most of the previously reported macrocycles exhibited mesophases at relatively high temperatures and with narrow temperature ranges. Except for the metal complexes of some macrocycles,[5c,d] we are not aware of any other examples of macrocyclic mesogens having such a wide temperature range for liquid crystallinity.

The growth of single crystals of cyclo[6]aramide[23] has proved to be highly challenging since their first report in 2004.[18] Fortunately, slowly evaporation of a solution of **4** in chloroform and ethanol (1:1, v/v) led to the formation of single crystals of this macrocycle,[15] that shares exactly the same backbone as **1a** but has shorter peripheral groups. This is one of the first crystal structures of these H-bonded aromatic oligoamide macrocycles with backbones enforced by three-center hydrogen bonds.[14d,22b] The diameter of the cavity measures 8.17 Å (Figure 4a), which is large enough to accommodate different guest molecules or ions. Interestingly, the macrocycle has a nearly flat backbone (Figure 4b), rather than the shallow bowl conformation previously predicted by computational studies.[19] The very small dihedral angle of 1.56° suggests almost perfect face-to-face π–π stacking between the macrocyclic aromatic backbones. The interplanar distance between two adjacent macrocycles is found to be 3.89 Å (Figure 4c), which is in good agreement with the intermolecular π–π stacking distance of 3.88 Å revealed by the XRD data of **1a**, and further suggests similar columnar stacking in the liquid-crystalline phases.

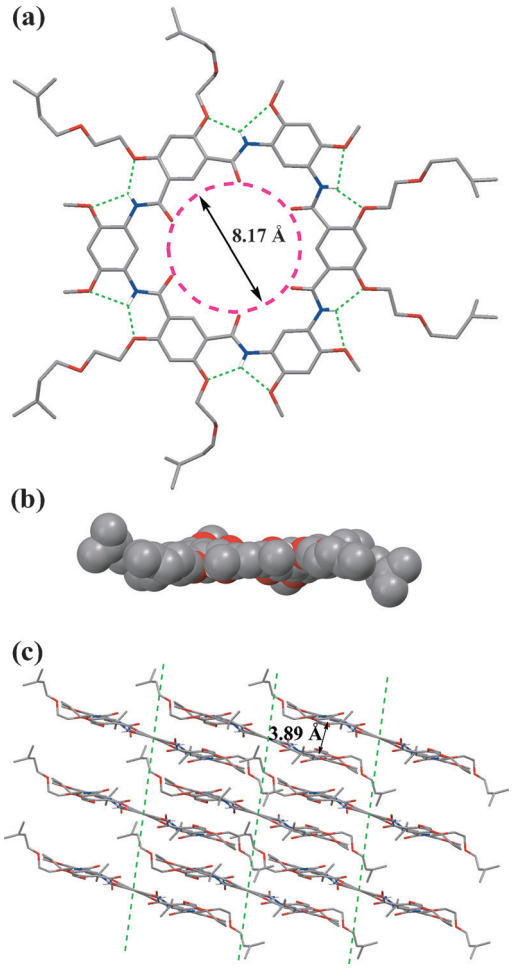

Figure 4. X-ray crystal structure of cyclo[6]aramide **4**. a) Top view, b) side view in the CPK model, illustrating a near-planar macrocyclic backbone, and c) molecular packing viewed along the a axis with the dashed green lines drawn passing through the cavities of the macrocycles. The dashed green lines in (a) indicate hydrogen bonds.

Inspired by our recent work on the strong binding of dialkylammonium salts by cyclo[6]aramides,[24] we probed the possibility of exploiting macrocyclic H–G interactions to additionally influence the LC process. First, the binding affinities of **1a**·DEA-HCl, **1a**·TEA-HCl, **1c**·DEA-HCl, and **1c**·TEA-HCl (DEA-HCl = diethylammonium chloride, TEA-HCl = triethylammonium chloride) were determined by ^{1}H NMR titration experiments and found to range from $(2.71 \pm 0.55) \times 10^3\,M^{-1}$ to $(9.10 \pm 2.08) \times 10^3\,M^{-1}$ in $CDCl_3$ (Table 1). These data show sufficiently strong binding abilities

Table 1: ^{1}H NMR titration data of the complexes at 298 K and XRD data of host–guest complexes (host:guest = 1:1).

System	Molar ratio[a]	$10^{-3} \times K_a$ [M^{-1}][b]	Range [°C][c]	Phase/T [°C][d]	*a* [Å]
1a	–	–	52	Col_h/160	26.85
1a·DEA-HCl	1:1	2.71 ± 0.55	69	Col_h/100	26.43
1a·TEA-HCl	1:1	4.55 ± 0.79	63	Col_h/180	26.57
1c	–	–	156	L_{col}/180	23.21
1c·DEA-HCl	1:1	4.15 ± 0.69	161	Col_h/100	27.14
1c·TEA-HCl	1:1	9.10 ± 2.08	140	Col_h/100	25.90

[a] The 1:1 stoichiometry of the complexes was established by the molar ratio method in $CDCl_3$. [b] The association constants K_a values were obtained by ^{1}H NMR titrations at 298 K in $CDCl_3$. [c] The temperature ranges of the mesophases were determined by DSC or POM based on the second heating cycle. [d] XRD measurement temperature.

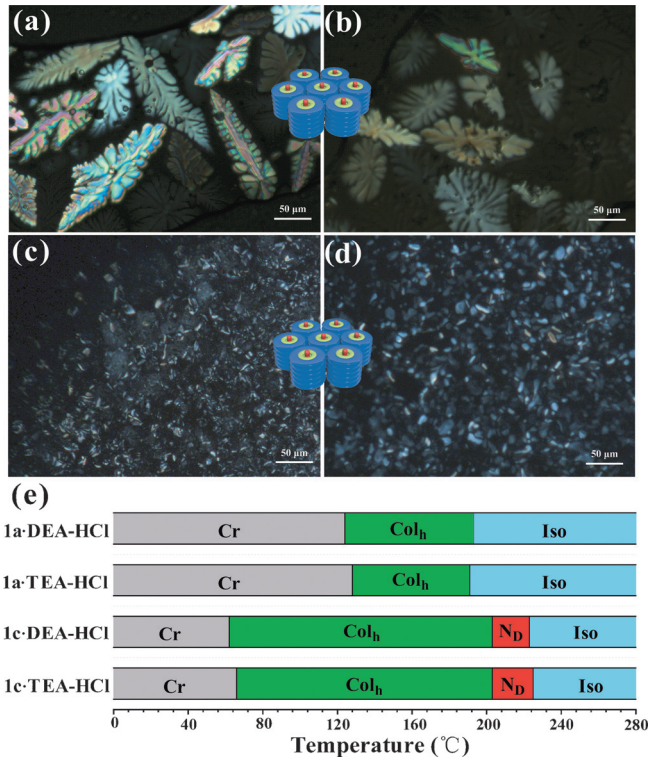

Figure 5. Polarized optical micrographs showing mesophases of a) **1a**·DEA-HCl at 100 °C (Col_h), b) **1a**·TEA-HCl at 150 °C (Col_h), c) **1c**·DEA-HCl at 100 °C (Col_h), and d) **1c**·TEA-HCl at 170 °C (Col_h) upon cooling from the isotropic melt. e) Phase diagrams of the complexes (host: guest = 1:1) traced during the heating cycle by POM with a heating rate of 2 °C min^{-1} by the addition of 1 molar equivalent of DEA-HCl or TEA-HCl. Scale bar in (a–d) = 50 μm.

of these macrocycles towards cationic guests. Accordingly DEA-HCl or TEA-HCl are added to a solution of **1a** or **1c** in chloroform, which is followed by solvent evaporation to afford the 1:1 complexes. Results from two-dimensional NOESY experiments suggest that alkylammonium ions are bound inside the cavity instead of locating around the periphery of **1a** or **1c** (Figure S59–83). Next, the H–G complexes were subjected to POM imaging. On cooling from the isotropic melt, clear dendritic (Figure 5a,b) or pseudo focal conic textures (Figure 5c,d) are observed, suggesting formation of columnar LC assemblies. For **1a**, forming a complex with organic salts only imparts a very limited effect upon the LC textures and phase diagrams (Figure 5e). Nevertheless and to our delight, a mesogenic transition occurs from the lamellar columnar phase (L_{col}) observed for **1c** to a more densely and well-organized hexagonal columnar phase (Col_h) for **1c**·TEA-HCl. A similar trend follows when DEA-HCl is used as the guest salt (Table 1). The XRD patterns of H–G complexes recorded at measurement temperatures (Figures S92, S93) also point to a transition from the L_{col} mesophase for uncomplexed **1c** to the Col_h mesophase for both H–G complexes **1c**·DEA-HCl and **1c**·TEA-HCl. Meanwhile, the Col_h mesophases of the complexes remain intact at varying molar ratios of host and guest as indicated by POM and DSC data (Figure S89–91). These unprecedented macrocyclic discotic LC phase transitions from a lamellar to hexagonal phase may arise from the electrostatic interaction and steric exclusion between adjacent macrocyclic cores containing bulky alkylammonium ions in the H–G complexes. The other two complexes **1d**·TEA-HCl and **1e**·TEA-HCl based on amphiphilic cyclo[6]aramides were also investigated (Figure S94–98, Tables S11 and 12), but the results failed to show any discernable change in mesophase transitions. Moreover, addition of a second component results in temperature ranges for **1a** and **1c**–**1e** that vary only within a narrow window of 10–17 °C (Table S13). This is partially rationalized by the fact that the guest is only trapped inside the cavity, thus producing a negligible effect upon the packing surroundings of macrocyclic molecules in a LC phase.

In conclusion, we have demonstrated the ability of cyclo[6]aramides **1a**–**1e** to serve as a new class of H-bonded macrocyclic mesogens that produce stable lamellar, discotic nematic, hexagonal, and rectangular mesophases over a very wide temperature range. The rich mesophases are readily achieved by incorporating side chains of different polarities and lengths. The organic-guest-triggered phase transition based on supramolecular H–G interactions involving the macrocyclic cavity offers a hitherto unexplored strategy for manipulating the properties of LC materials. Further structural variations around the exterior of these mesogenic macrocycles are expected to create new LC materials with novel thermal and chemical responsiveness.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (21172158), the Doctoral Program of the Ministry of Education of China (20130181110023), the National Science Foundation for Fostering Talents in Basic Research of the National Natural Science Foundation of China (J1210004 and J1103315), the Open Project of the State Key Laboratory of Supramolecular Structure and Materials (SKLSSM2015026), the Open Project of the State Key Laboratory of Structural Chemistry (20140013), and the US National Science Foundation (CHE-1445742 and CBET-1512164). The Comprehensive Training Platform of the Specialized Laboratory, College of Chemistry, Sichuan University, is acknowledged for NMR and FTIR analyses.

Keywords: host–guest systems · liquid crystals · macrocycles · mesogens · mesophase transitions

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 11147–11152
Angew. Chem. **2015**, *127*, 11299–11304

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[15] CCDC 1400074 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Received: June 9, 2015
Published online: August 11, 2015

