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Triangular arylene ethynylene macrocycles: syntheses, optical, and thermotropic liquid crystalline properties[†]

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A series of triangular, shape-persistent arylene–ethynylene macrocycles (AEMs) of related structures were synthesized and studied, with a focus on their mesomorphic behavior in correlation with their chemical structure. Generally, these discotic molecules decorated with flexible side chains demonstrated a propensity to form thermotropic liquid-crystalline (LC) phases. Characterized by differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction (XRD), four of the eight investigated macrocycles manifested thermodynamically stable mesophases, featuring discotic nematic or columnar structures. Longer alkyl side chains were found more conducive to mesophases, and the alkoxycarbonyl functionality was a more effective side-chain linkage at inducing and stabilizing the LC states than the alkoxy side group. The size and structure of the cyclic aromatic backbone influenced both the occurrence and type of mesophase exhibited.

Introduction

Conjugated organic molecules emerged as a type of versatile functional material due to their appealing electronic and optical properties.^{1,2} Recently, both theoretical and experimental investigations have revealed that, in addition to geometry and chemical structure of the molecules, the molecular packing motif strongly influences the charge-carrier mobility of the system.³⁻⁵ To achieve optimal device performance, the ability to form supramolecular structures with long-range order, facilitating energy or carrier transport, is one of the critical issues that need to be addressed.³ The presence of liquid-crystalline (LC) phases is considered a desirable property for organic semiconductive molecules, especially for solution-processed systems. This is because owning to the fluid and dynamic nature, LC materials are capable of minimizing and self-healing structural defects (e.g., grain boundaries) while spontaneously forming ordered structures of micro- to macroscopic dimensions.⁴ Columnar phases are considered particularly favorable for semiconductivity applications, as intermolecular electronic coupling effected through molecular orbital overlapping is most efficient in columnar architectures and one-dimensional charge-carrier transport is thereby vastly facilitated.5

Molecules of a planar, shape-persistent (*i.e.*, discotic) central core decorated with flexible side chains at the periphery are most

favorable for columnar LC phase formation. The discotic mesogens, typically π -conjugated aromatic skeletons, possess a distinct tendency to stack face-to-face into columns, which are phase-segregated from the side chains driven by intermolecular forces such as aromatic stacking, van der Waals, hydrophobic interactions, and so on. Hierarchically ordered supramolecular architectures of various organization patterns have been observed with such columns through self-assembly. So far, the most intensively studied discotic core structures include substituted benzene,⁶ triphenylene,⁷ perylene⁸ and coronene^{54,9} derivatives, porphyrin and phthalocyanine derivatives,¹⁰ macrocycles,¹¹ *etc.* Systems featuring metal–ligand coordination,¹² dipole–dipole,¹³ hydrogen bonding,¹⁴ or donor–acceptor¹⁵ interactions have also been reported.

For discotic molecules, it is known that the interplay and balance of the rigidity of the core and flexibility of the side chains play a pivotal role in governing the LC properties. Specifically, studies with a wide range of molecules manifesting various discotic LC phases showed that a number of structural attributes are critical for determining the LC state characteristics,⁴ including the chemical structure, size, geometry, and symmetry of the aromatic core, the length, number, and structure of side chains, as well as the functional linkage connecting the core with the side chains. With regard to the complexity of the influential factors, systematic investigations are warranted for a better understanding of the correlation between the molecular structure and LC phases characteristics, and relevant knowledge is indispensable for designing new molecules that exhibit both LC states and optimal semiconductive properties.

Among various discotic LC mesogens, shape-persistent macrocycles represent a unique group.^{16–19} Syntheses and characterizations of shape-persistent macrocycles have been conducted for

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decades.^{20,21} Having a unique interior void, these macrocycles feature a nano-sized tubular cavity when assembling into columnar arrangements. Intra-annularly functionalized nanotubes have been designed and exploited for a variety of purposes, including host-guest interactions, covalent organic frameworks, light-harvesting systems, sensors, and so on.²² Nonetheless, up till now only limited examples of shape-persistent macrocycles manifesting discotic LC phases have been reported. Moore and coworkers first studied a set of phenylene-ethynylene macrocycles with different peripheral substitutions exhibiting columnar phases.¹⁶ Höger's research group demonstrated that AEMs with the interior occupied with alkyl side chains gave rise to discotic nematic or columnar phases.¹⁷ Tew introduced two types of side chains of different polarity to ortho-phenylene ethynylene macrocycles, both displayed LC phases.¹⁸ Kato et al. reported a discotic LC AEM having glutamic acid and alkyl side chains on the exterior and oligoethylene glycol side chains in the interior.¹⁹ However, precedents of AEMs that exhibit both electronic functions and discotic LC phases have been rarely reported.

Recently, we studied a triangle-shaped AEM that displayed an extraordinary photoconducting capacity.^{23a} To further investigate pertinent functions and explore the applications of such macrocycles, we subsequently designed and synthesized a series of AEMs of related structures (Chart 1, 1–8). Here we report a study on the correlation between the molecular structure and LC properties by systematically varying the chemical features of the macrocycles. Specifically, the influences of side chains, size and structure of the aromatic skeleton, as well as the linkage joining the side chains with the shape-persistent core were examined.

Results

Chemical structures and syntheses of the AEMs

Chemical structures of all investigated AEMs in this study are depicted in Chart 1. The previously reported AEMs 1^{23a} and 2^{23b} had the same cyclic framework of oligo(*o*-phenyleneethynylene*alt-p*-phenyleneethynylene). AEMs **3** and **4** had an identical backbone, which comprised three 4,4'-biphenylene units connected by three *o*-phenylene bis(ethynylene) groups. Whereas in AEMs **5** and **6**, the triangular scaffold was constituted by 3,6phenanthrylene bis(ethynylene) units in combination with *p*-phenylene groups. All AEMs **1–6** had six alkoxy side chains attached to the cyclic backbone, two on each vertex of the triangle. Each pair of macrocycles with the same backbone differed by the length of the side chains. Hexyloxy side chains were attached to AEMs **1**, **3**, and **5**, while longer dodecyloxy side chains were tethered to AEMs **2**, **4** and **6**.

To unravel the effect of side chain linkage on the LC properties, we also designed two other triangular AEMs with carboxylic ester-linked side chains, *i.e.*, macrocycles **7** and **8**. Both of these macrocycles had a cyclic oligo(*o*-phenyleneethynylene-*alt-p*phenyleneethynylene) backbone. In AEM **7**, each of the three *o*-phenylene units was tethered with a hexyloxy side chain *via* a carbonyl linker.²⁴ AEM **8** adopted the same ester side-chain linkages, but this molecule was decorated with six hexyloxy carbonyl groups, one on each of the *o*- and *p*-phenylene units.

An overview of the synthetic routes to AEMs 1–8 is illustrated in Scheme 1 (see the ESI for synthetic details[†]). Two different cyclization strategies were employed to obtain the eight target



Chart 1 Chemical structures of studied AEMs.

macrocycles.²⁰ AEMs 1 to 6 were realized via route 1, in which the final step was designed to couple two different short, open-chain precursors into a cyclic structure under relatively dilute conditions. One of the two fragments had aryliodide functionality on both ends, and the other was terminated with two acetylene groups. The two molecules were coupled into a macrocycle via two consecutive Sonogashira-Hagihara reactions in one pot, i.e., an intermolecular cross-coupling followed by an intramolecular ring-closure reaction. The evident advantage of this cyclization protocol was the shorter synthetic route (compared to route 2), which compensated for the relatively low yield of the final step. But such a double cross-coupling method was only suitable for symmetrical macrocycles, like AEMs 1-6. Due to the lower symmetry of AEMs 7 and 8 (C_{3h}), a different synthetic scheme was designed. In route 2, the reactant for the final step was a longer oligomer containing all subunits that needed to be cyclized. The oligomer chain ends were asymmetrically functionalized with aryliodide and terminal ethynylene respectively, which were then

intramolecularly cross-coupled to accomplish the cyclization. Synthetic route 2 was apparently more sophisticated and tedious than route 1, for preparing the longer cyclization precursor. Employment of protective/masking groups was necessary to ensure the compatible accommodation of two complementarily reactive functional groups. Nonetheless, the yield of the final cyclization step was typically superior to that of route 1. Furthermore, the sequence of repeating units in the backbone could be precisely controlled *via* route 2. Upon the completion of syntheses, the structures of AEMs **1–8** were characterized and confirmed by ¹H and ¹³C NMR spectra, mass spectroscopy, and elemental analyses (see the Experimental Section).

Optical characterizations in solution

The absorption and emission spectra of AEMs **1–8** were recorded in dichloromethane solutions (Fig. S1[†]) and relevant data are summarized in Table 1. Generally, macrocycles of the same







Reagents and conditions: a) Pd(PPh₃)₄, Cul, Et₃N; b) CH₃I, 140 °C; c) K₂CO₃, CH₃OH, CH₂CI₂

Scheme 1 Synthetic schemes for AEMs 1-8.

backbone structure and side-chain linkers generated very similar spectra. The difference in side-chain length had negligible effect on the electronic spectra. However, alteration of the backbone structure evidently affected both the band shape and transition energy. Specifically, from the spectra of AEMs 1-6, it was clearly seen that variation of the side-chain length did not change the absorption maxima but slightly changed the fluorescence properties. All macrocycles displayed two major peaks in their emission spectra. The one of shorter wavelength was hardly affected by the side-chain length, while the one of longer wavelength exhibited a bathochromic shift of 2-3 nm upon extension of the side chains. When the *p*-phenylene units were replaced with 4,4'biphenylene groups, the absorption band and the lower-energy emission peak manifested noticeable hypsochromic shifts, suggesting that the dihedral angle between the two phenyl rings in the biphenylene units slightly disrupted the conjugation. On the other hand, switching the triangle vertex from o-phenylene to 3,6-phenanthrylene group brought about a perceptible bathochromic shift in the absorption maxima but a minor blue shift of the emission band. This result indicated that the 3,6-phenanthrylene unit was slightly more effective at narrowing the band gap than the o-phenylene group, while the smaller Stokes shift was attributed to the rigidity of the phenanthrylene moiety. The effect of side-chain linker was inferred by comparing the spectra of AEMs 1 and 7. It was noted that changing the dialkoxy to single alkyl carboxylate side chain resulted in a hypsochromic shift in both absorption and emission spectra, by approximately 10 and 20 nm, respectively. However, when additional carboxylate groups were attached to the *p*-phenylene groups on each side of the triangle, bathochromic shifts occurred with both the absorption and emission spectra, as illustrated by AEM 8. These results revealed that attaching carboxylate groups to different positions of the conjugated cyclic backbone had varied consequences in electronic transitions.

Thermotropic properties

The thermal stabilities of all studied AEMs were analyzed by thermogravimetric analysis (TGA) under a nitrogen atmosphere, and subsequent characterizations were carried out below their respective decomposition temperatures. The thermal transitions exhibited by the macrocycles were characterized by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). Phase transition temperatures and corresponding

Table 1 Optical properties of AEMs 1-8^a

	Absorbance λ_{max} (nm)	Extinction coefficient (L mol ⁻¹ cm ⁻¹)	Emission λ_{max} (nm)
1	358	1.8	427, 453
2	358	1.4	428, 455
3	353	1.3	427, 449
4	353	1.7	426, 452
5	366	1.9	422, 446
6	366	1.9	423, 449
7	346	1.6	406, 433
8	351	1.5	413, 439

 a Spectra were recorded at room temperature in CH2Cl2 at ca. 5×10^{-6} mol $L^{-1}.$

enthalpy changes were determined based on the DSC measurements. For certain transitions with a small enthalpy change undetectable by DSC, the transition temperatures were determined based on the POM observations. The mesophase structures were revealed by the variable-temperature X-ray diffraction (XRD) measurements, in combination with information provided by POM. Samples for DSC and XRD characterizations were obtained as precipitates from mixed solvents of dichloromethane and ethanol, while thin films drop-cast from dichloromethane solutions were used for POM characterizations. All thermotropic phase transition results are summarized in Table 2, and the mesophase structure data are listed in Table 3.

The properties of macrocycle **1** were first examined. As the selfassembled structures of this molecule obtained from solution was previously reported to exhibit optimal photoconductivity, which was lost upon thermal annealing,^{33a} its behavior prior to thermal treatment was also investigated. The crystalline sample precipitated from solution displayed multiple transitions during the first heating cycle, as shown by DSC (Fig. S2†). Interestingly, a unique monotropic mesophase was observed in this process (see detailed characterizations in the ESI†). Nonetheless, all thermal transitions observed in the first heating cycle were irreversible. In the cooling scan, only one exothermic peak was detected at 196 °C by DSC, which was confirmed by XRD to be a transition from the isotropic liquid to a crystalline phase. This crystal structure directly melted into the isotropic state at 210 °C (Fig. S4†).

AEM 2 had an identical cyclic backbone with that of AEM 1, but longer dodecyloxy side chains were attached to it. During the first heating scan, the solution-processed sample of SEM 2 also exhibited a metastable LC phase, in a relatively wide temperature range between 65 and 170 °C (Fig. S8†). A typical spherulitic texture was observed under POM, which identified the hexagonal columnar structure (Fig. S9†). Nonetheless, the LC structure was not reproduced during the cooling or second heating cycle. Instead, an amorphous state with a glass transition was observed (Fig. S10–S13†).

AEM 3 displayed no LC mesophase. In DSC traces, only a crystal-to-crystal transition was observed at 215 °C during the first heating scan, and no thermal transition was detected in subsequent cooling and heating cycles (Fig. S14†) before the compound decomposed at 372 °C.

Keeping the same oligo(o-phenyleneethynylene-alt-biphenyleneethynylene) backbone structure, when the side chains were changed to longer dodecyloxy groups, AEM 4 exhibited a rectangular columnar LC phase (Fig. 1). The crystalline sample precipitated from solution exhibited a melting point and entered a LC phase at 164 °C, which went isotropic at 198 °C (Fig. S15†). During the cooling cycle, the isotropic liquid was slightly supercooled and the LC phase appeared at 190 °C. A much lower crystallizing temperature of 42 °C was observed, giving rise to a structure different to that obtained from solution but similar to that in the LC state (Fig. S18[†]). The DSC traces became reversible after the second heating cycle. For this molecule, the crystallization and melting processes took place with very small enthalpy changes, although the transition was discernible from the change of birefringent texture under POM (Fig. S19[†]). On the other hand, the LC-isotropic transition was accompanied with a significant enthalpy change, suggesting a relatively

 Table 2
 Phase transition temperatures and enthalpy data

	Transition $T/^{\circ}$ C (enthalpy/kJ mol ⁻¹) ^{<i>a</i>}		
AEM	1st cooling	2nd heating	
1	Iso 196 (-18.3) \rightarrow Cr	Cr 210 (20.7) \rightarrow Iso	
2	Iso $156 (-1.8) \rightarrow O - 16 (-2.7) \rightarrow G$	$G - 11 (2.7) \rightarrow O 164 (2.7) \rightarrow Iso$	
4	Iso $190(-27.3) \rightarrow \text{Col}_{rd} 42(-0.5) \rightarrow \text{Cr}$	$Cr 58 (0.4) \rightarrow Col_{rd} 197 (27.9) \rightarrow Iso$	
6	Iso $195^b \rightarrow N_D 162 (-34.1) \rightarrow O$	$O 169 (34.2) \rightarrow N_D 198^b \rightarrow Iso$	
7	Iso $177 (-12.4) \rightarrow \text{Col}_{rd} 156 (-10.3) \rightarrow \text{Cr}$	$\operatorname{Cr} 177(11.2) \rightarrow \operatorname{Col}_{rd} 186(7.0) \rightarrow \operatorname{N}_{D} 191^{b} \rightarrow \operatorname{Isc}$	
8	$\operatorname{Col}_{\operatorname{ho}} 81 \ (-13.8) \to \operatorname{Cr}^{12}$	Cr 141 (19.7) \rightarrow Col _{ho} \rightarrow 335 (dec.) ^c	
^{<i>a</i>} Data were obtain hexagonal: Col. –	ined from DSC analyses at a scan rate of 5 °C min ⁻¹ ; Cr = crystal r	whase; $O =$ amorphous state; $G =$ glass state; $Col_h =$ columnation $Col_h = -$ decomposition temperature	

hexagonal; Col_r = columnar rectangular (d = disordered; o = ordered); Iso = isotropic; N_D = discotic nematic; dec. = decomposition temperature. ^b The transition was only observed with POM and XRD.^c The temperature corresponds to 5% weight loss in TGA measurement at a heating rate of 10 °C min⁻¹.

ordered mesophase but poorly organized crystalline structure. These characteristics were consistent with the XRD patterns collected from respective phases. Sharp peaks were detected in the LC phase while poorly resolved diffractions emerged from the crystalline state. The XRD profile of the LC state revealed a series of diffractions corresponding to (200), (110), and (210) of a rectangular columnar phase (Fig. 1d). Since no diffraction was observed from plane (001), this mesophase was considered disordered along the main axis of the columns. The presence of a diffraction with the Miller index matching (h + k = 2n + 1) excluded the *c2mm* symmetry, so the Col_r phase was identified to be of *p2gg* symmetry.²⁵ The broken fan-like texture observed under POM in the LC temperature range also corroborated the rectangular columnar feature (Fig. 1b and 1c).

For AEM 5 with a cyclic backbone composed of alternative *p*phenyleneethynylene and 3,6-phenanthryleneethnylene units decorated with short hexyloxy side chains, no mesophase was observed in repeated heating and cooling cycles between 0 and 250 °C. Different crystal-to-crystal phase transitions were observed by DSC during the first and second heating scans (Fig. S20 and S21†), revealing the effect of solution-processing on the sample.

On the other hand, the analogous AEM 6 having the same backbone but longer side chains exhibited a discotic nematic (N_D) phase (Fig. 2). Upon heating the compound to 169 °C, a Schlieren texture characteristic of the nematic phase was observed under POM (Fig. 2b). The recorded WAXD pattern confirmed the nematic phase by showing only one diffuse peak in the wide-angle regime (Fig. 2c). DSC clearly revealed the transition to the LC phase with a distinct endothermic peak, but the transition to the isotropic state was not detectable by monitoring the heat flow (Fig. S23 and S24[†]). A small enthalpy change is typical for the transition between nematic and isotropic states, consistent with the minimal degree of order in the nematic phase. As the birefringent Schlieren texture disappeared at ca. 198 °C upon heating, the clearing point was identified based on the POM observations. For this molecule, nearly identical DSC traces were obtained from the first and second heating scans. This observation indicated that AEM 6 formed similar molecular structures from solution and upon thermal treatment.

AEM 7 was a macrocycle with an oligio(*o*-phenyleneethynylene-*alt-p*-phenyleneethynylene) backbone. Instead of dialkoxy side chains, each of the three *o*-phenylene units was attached with a hexyl carboxylate group, making the molecule of

Table 3	X-Ray	diffraction	data
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AEM	Phase (lattice parameters)	Miller indices (hkl)	$d_{\exp}^{a}(d_{calcd})$ (Å)	r/R (Å) ^b
4	$\text{Col}_{\text{rd}} (a = 81.6 \text{ Å}, b = 36.1 \text{ Å})$	(200)	40.8	21/53
		(110)	33.0	
		(210)	27.1 (27.0)	
6	ND			19/51
7	$\tilde{\text{Col}}_{rd}$ (a = 54.1 Å, b = 27.9 Å)	(200)	27.1	16/32
		(110)	24.8	
		(310)	15.0 (15.1)	
		(020)	13.9 (14.0)	
		(620)	7.6 (7.6)	
		(040)	7.0 (7.0)	
	ND		31.0	
8	$\bar{\text{Col}}_{\text{ho}}$ (a = 27.4 Å, c = 3.6 Å)	(100)	23.7	16/32
		(110)	13.7 (13.7)	
		(200)	11.9 (11.9)	
		(210)	8.9 (8.9)	
		(001)	3.6	

^{*a*} Data were determined based on diffractions in XRD profiles. ^{*b*} r represents the calculated radius of the shape-persistent cyclic framework and R represents the calculated molecular radius of the macrocycle including side chains in the extended conformation (data were estimated based on B3LYP/6-31G calculations, *cf*. Fig. S40, ESI).



Fig. 1 (a) DSC traces of AEM **4** at a rate of 5 °C min⁻¹; (b) optical microscopic images of AEM **4** at 188 °C during the 1st heating scan and (c) at 90 °C in the cooling cycle (under crossed polarizers, $\times 200$); (d) XRD pattern of **4** at 100 °C during the cooling scan (the asterisks indicate diffractions from the aluminum foil used for supporting the sample); (e) a schematic representation of the rectangular columnar packing with lattice constants indicated.

 C_{3h} symmetry. Based on the combined characterization results of POM, DSC, and XRD, two different mesophases were identified with this macrocycle (Fig. 3). Upon heating a sample precipitated from solution, a crystal-to-crystal transition was first displayed at *ca.* 148 °C (Fig. S26†). This transition manifested itself as a large endothermic peak in the DSC trace. Subsequently, two more endothermic peaks occurred at higher temperatures of 176



Fig. 2 (a) DSC traces of AEM **6** at a rate of 5 °C min⁻¹; (b) optical microscopic image of AEM **6** showing a *Schlieren* texture characteristic of nematic phase (at 184 °C under crossed polarizers, \times 400); (c) WAXD profile of AEM **6** at 180 °C in the cooling cycle.

and 187 °C, respectively. Different LC textures were observed below and above the latter temperature under POM. Between 176 and 187 °C, a pseudo-focal conic fan-shape texture appeared, which gradually transformed into the Schlieren texture at 187 °C (Fig. 3b and 3c). XRD confirmed the first mesophase to be a rectangular columnar phase (Col_{rd}) by showing multiple diffractions of (200), (110), (310), (020), etc. (Fig. 3d). Again, no diffraction was detected along the main axis of the columns, suggesting disorder in that direction. The other mesophase displaying the Schlieren texture was assigned to the discotic nematic phase (N_D) . Only one diffuse peak in the small-angle region was detected by XRD in the nematic phase, with a *d*-spacing correlated to the size of the macrocycle. Again, the clearing temperature around 191 °C was only detected by POM but not DSC. Thus, the N_D phase had a very narrow temperature range. In the cooling process, the N_D phase was not observed and only the Col_r phase was detected. Evidently, the narrow nematic phase was easily masked by even slightly super-cooled isotropic state. For AEM 7, the DSC trace of the first heating scan was mostly reproduced in subsequent cooling and heating scans, except for the large enthalpy change of the crystal-to-crystal transition, which disappeared in subsequent scans (Fig. S27 and S28†). These results indicated that, although a minor solution-processing effect persisted with this macrocycle, the two mesophases manifested were thermodynamically stable states.



Fig. 3 (a) DSC traces of AEM 7 at a scan rate of 5 °C min⁻¹; optical microscopic images of AEM 7 showing textures characteristic of Col_r and N phases at (b) 180 °C and (c) 190 °C, respectively (under crossed polarizers, ×200); (d) XRD pattern of AEM 7 at 170 °C in the 1st cooling cycle.

AEM 8 possessed an identical aromatic backbone with that of AEM 7 and was also of C_{3h} symmetry, but it had an ester-linked hexyl side chain tethered to each of the six phenylene rings. Such a structural modification gave rise to rather distinct thermotropic behavior from that of 7. AEM 8 manifested a very stable columnar LC phase with a wide temperature range. Based on the DSC results (Fig. 4a), the onset of the mesophase emerged at 141 °C and no isotropic state was observed before the molecule decomposed at 335 °C. In the cooling process, the mesophase was significantly super-cooled and crystallized at 81 °C. Under the POM, fan-like LC textures were observed to coexist with large areas of homeotropic domains in the mesophase, suggesting a preferred uniaxial alignment of the columns (Fig. 4b). The

XRD profile showed multiple peaks in the small-angle region in the LC state, in accordance with diffractions of (100), (110), (200), and (210) in a hexagonal columnar phase (Fig. 4c and 4d).^{26,27} Additionally, a diffraction corresponding to a *d*-spacing of 3.6 Å was identified with this macrocycle in the wide-angle region, and it was clearly attributable to the π - π stacking distance of the aromatic cores. Hence, of all the AEMs investigated in this study. AEM 8 was the only one that exhibited an ordered columnar phase displaying the (001) diffraction peak. This peak was relatively sharp at lower temperatures and became somewhat diffused as the temperature was elevated. In the meanwhile, the diffraction peaks in the small-angle regime were slightly shifted to longer d-spacing values (Fig. S33[†]). These observations were indicative of certain extent of loosening of the hexagonal lattice, along with reduced order in the π - π stacking dimension at increased temperatures. A very similar hexagonal columnar structure was observed with the crystalline state. No signature of solution processing history was demonstrated by this molecule, as shown by the completely reproduced DSC traces recorded in the first and subsequent heating cycles (Fig. S30[†]).



Fig. 4 (a) DSC traces of AEM **8** at a rate of 5 $^{\circ}$ C min⁻¹; (b) optical microscopic image of AEM **8** (at 170 $^{\circ}$ C under crossed polarizers, ×200); (c) WAXD of AEM **8** at 180 $^{\circ}$ C in the 1st cooling cycle; (d) a schematic representation of the molecular packing in the discotic hexagonal columnar phase.

Discussion

Generally, the designed triangular AEMs exhibited a distinct propensity to form LC phases (Fig. 5). The current study confirmed that the side chains were pivotal for LC state occurrence. Longer alkyl chains were much more favorable for the mesomorphic behavior. Among AEMs 3-6, neither 3 nor 5 with shorter hexyloxy groups exhibited mesophases, whereas both analogous AEMs with longer dodecyloxy side chains (i.e., 4 and 6) manifested LC phases. In addition to the side chain length, the functional group joining the backbone with side chains also played a critical role in governing the LC properties. Unlike AEMs with hexyloxy side chains, both macrocycles having esterlinked short hexyl groups (7 and 8) displayed mesophases. Evidently, the ester linkage was more effective at inducing the LC phases. It is known that the more polar and electron-withdrawing carbonyl group is capable of bringing about stronger intermolecular π - π stacking interactions.¹⁶ Also, compared with the ether linker, the carbonyl group was in conjugation with the aromatic skeleton, facilitating a more extended, planar framework, which not only further strengthened the interactions among mesogens but possibly allowed for a great extent of lateral molecular mobility while maintaining significant attractive intermolecular forces.

By comparing the properties of macrocycles 2, 4, and 6, information regarding the effect of the aromatic backbone on the LC state was unravelled. The fact that AEM 2 possessed an amorphous state whereas AEM 4 formed a Col_r arrangement suggested that enlargement of the triangular mesogen by replacing the *p*-phenylene unit with biphenylene group favored mesophase formation, likely resulting from stronger intermolecular and inter-columnar interactions in AEM 4. Expanding the core structure in a different fashion led to disparate consequences. AEM 6 on the other hand manifested a narrow N_D phase. The melting point of AEM 6 was much higher than that of AEM 4, but the clearing point was similar, thus showing a considerably compressed LC-phase temperature range. These observations indicated that the aromatic surface and structure had a pronounced effect on mesophase formation. The type of mesophase was also strongly dependent on the chemical features of the aromatic backbone.

Additional information was obtained by comparing the properties of AEMs 7 and 8. AEM 8 possessed a much more



Fig. 5 LC phase temperature ranges of studied AEMs (based on data from the second heating cycle).

stable columnar mesophase, featuring hexagonally arranged columns of stacked macrocycles. This LC state exhibited a lower melting point and a much higher clearing point than AEM 7. The extraordinary stability of the LC phase was very likely related to the presence of a greater number of ester functionalities, the inclusion of which was rather effective at promoting the mesophase. Imaginably, with more ester-linked side chains, intermolecular interactions were further strengthened, which is consistent with a significantly elevated LC-to-isotropic transition temperature of AEM 8 compared to that of AEM 7. However, the fact that macrocycle 7 manifested a Col_r phase (even though within a very narrow temperature range) before entering the N_{D} state while AEM 8 exhibited a Col_h phase led to the proposition that core-core correlation among different columns was suppressed in AEM 8 relative to that in AEM 7. This notion was related the presence of side chains appended to the *p*-phenylene rings. Imaginably, the additional side chains of AEM 8 may allow a greater magnitude of rotational motion of the macrocycles around the main axis of the columns without significantly disrupting the interactions among side chains of different molecules. Such motions likely resulted in reduced directionality of molecular orientation with respect to neighboring columns. It was also considered that since AEM 8 was the only macrocycle studied herein that displayed order along the columns, this phenomenon might also be correlated to the side chains on the p-phenylene rings. These side chains possibly prohibited the rotation of the *p*-phenylene units around the ethynylene groups, by imparting stronger aromatic stacking interactions, and more importantly intermolecular interactions among side chains. Such rotational motions of the *p*-phenylene groups, which might exist in all other macrocycles, likely hampered ordered stacking of the molecules within columns.

Experimental section

Methods and materials

All chemicals were used as received unless otherwise indicated. Oxygen or moisture sensitive reactions were performed under a nitrogen atmosphere using the standard Schlenk technique. Reagent-grade tetrahydrofuran (THF) was distilled over sodium and benzophenone, toluene was distilled over sodium, diisopropylamine and triethylamine were distilled over CaH₂ prior to use. NMR spectra were recorded on a Varian Mercury 200 (200 MHz), Mercury plus 300 (300 MHz), or Bruker ARX 400 (400 MHz) instrument, using CDCl₃ as the solvent. Chemical shifts were reported in parts per million (ppm) relative to TMS (0 ppm) or CDCl₃ (77.0 ppm) for ¹H and ¹³C NMR spectra, respectively. FTMS were recorded on a Bruker APEX IV mass spectrometer. MALDI-TOF was recorded on a Bruker Daltonics Inc. BIFLEX III mass spectrometer. Elemental analyses were performed using a German Vario EL III elemental analyzer.

UV-Vis absorption spectra were recorded on a Hitachi U-4100 spectrophotometer using 1-cm quartz cuvettes. Photoluminescence spectra were recorded on a Horiba Jobin Yvon FluoroMax-4P spectrofluorometer in the right-angle geometry and using 1 cm quartz cuvettes. Thermal stability of the AEMs was studied using a TA Q600 SDT instrument at a heating rate of 10 K min⁻¹ under a N₂ atmosphere. The thermal properties were characterized with a TA Q100 DSC calorimeter under a N₂ atmosphere. The temperature and heat flow were calibrated at varied heating and cooling rates using standard materials. Phase transitions were also examined by Leica DML polarized optical microscope (POM) with a Mettler hot stage (FP-90) with samples contained in N2 atmosphere. The XRD experiments were performed with a high flux SAXS instrument (SAXSess, Anton Paar) equipped with Kratky block-collimation system (the qrange covered by the IP was from 0.06 to 29 nm⁻¹, $q = 4\pi (\sin\theta)/\lambda$, where the wavelength λ was 0.1542 nm and θ was the scattering angle). A temperature control unit (Anton Paar TCS300) in conjunction with the SAXSess was utilized to study the structure evolution as a function of temperature. The temperaturedependent 1D WAXD measurements were performed with a Rigaku MultiFlex 2 kW tube-anode X-ray (Cu-Ka radiation) generator coupled to a diffractometer at a scanning rate of 1° min⁻¹. The peak positions were calibrated using silicon powder in the high-angle region (>15°) and silver behenate in the low-angle region (<15°). Background scattering was subtracted.

AEM structure characterizations

AEMs 1 and 2 were synthesized as previously reported.^{23ab} Structure characterization results of all other AEMs are as follows.

AEM 3 ¹H NMR (300 MHz, CDCl₃). δ 7.67 (24H, s), 7.05 (6H, s), 4.05 (12H, t, J = 6.6 Hz), 1.86 (12H, m), 1.55–1.35 (36H, m), 0.93 (18H, t, J = 7.2 Hz). ¹³C NMR (50 MHz, CDCl₃): δ 149.3, 139.5, 131.9, 126.8, 122.9, 118.7, 115.9, 91.9, 89.7, 69.2, 31.6, 29.1, 25.7, 22.6, 14.0. FTMS: Calcd for. C₁₀₂H₁₀₈O₆: 1429.8 (*m*/*z*). Found: 1452.8 (M + Na⁺). Found: C, 85.31; H, 7.66. Calc. for C₁₀₂H₁₀₈O₆: C, 85.67; H, 7.61.

AEM 4 'H NMR (300 MHz, CDCl₃). δ 7.68 (24H, s), 7.06 (6H, s), 4.06 (12H, t, J = 6.6 Hz), 1.86 (12H, m), 1.55–1.26 (108H, m), 0.89 (18H, t, J = 6.6 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 149.4, 139.7, 132.0, 126.9, 123.1, 118.8, 116.1, 92.0, 89.8, 69.4, 32.0, 31.5, 30.3, 29.71, 29.66, 29.42, 29.38, 29.2, 26.1, 22.7, 14.1. FTMS: Calc. for C₁₃₈H₁₈₀O₆: 1934.4 (*m*/*z*). Found: 1957.4 (M + Na⁺). Found: C, 85.51; H, 9.19. Calc. for C₁₃₈H₁₈₀O₆: C, 85.66; H, 9.38.

AEM 5 ¹H NMR (300 MHz, CDCl₃). δ 8.77 (6H, s), 8.11 (6H, d, J = 8.4 Hz) 7.65 (6H, d, J = 8.4 Hz) 7.63 (12H, s), 4.21(12H, t, J = 6.6 Hz), 1.92 (12H, m), 1.59–1.40 (36H, m), 0.96 (18H, t, J = 6.9 Hz). ¹³C NMR (75 MHz, CDCl₃): δ 143.8, 131.6, 129.3, 127.7, 126.5, 123.1, 122.3, 120.4, 92.1, 89.9, 73.7, 31.8, 30.5, 26.0, 22.7, 14.1. FTMS: Calc. for C₁₀₈H₁₀₈O₆: 1501.8 (*m*/*z*). Found: 1501.8 (*m*/*z*). Found: 86.45; 7.26. Calc. for C₁₀₈H₁₀₈O₆: C, 86.36; H, 7.25.

AEM 6 'H NMR (300 MHz, CDCl₃). δ 8.81 (6H, s), 8.15 (6H, d, J = 8.4 Hz) 7.69 (6H, d, J = 8.4 Hz) 7.65 (12H, s), 4.21(12H, t, J = 6.6 Hz), 1.92 (12H, m), 1.57–1.29 (108H, m), 0.90 (18H, t, J = 6.6 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 144.0, 131.7, 129.6, 129.5, 127.9, 126.6, 123.2, 122.5, 120.5, 92.1, 90.0, 73.8, 32.0, 30.6, 29.8, 29.7, 29.6, 29.4, 26.3, 22.7, 14.1. MALDI-TOF MS:

Calc. for C₁₄₄H₁₈₀O₆: 2006.4 (*m*/*z*). Found: 2006.8 (*m*/*z*). Found: C, 85.96; H, 8.99. Calc. for C₁₄₄H₁₈₀O₆: C, 86.18; H, 9.04.

AEM 7 ¹**H NMR (300 MHz, CDCl₃).** δ 8.04 (3H, d, J = 1.7 Hz), 7.78 (3H, dd, J = 8.7, 1.7 Hz), 7.51 (15H, m), 4.30 (6H, t, J = 6.8 Hz), 1.79 (6H, m), 1.55–1.30 (18H, m), 0.93 (9H, t, J = 6.9 Hz). ¹³C NMR (50 MHz, CDCl₃): δ 165.2, 132.8, 131.6, 131.5, 131.3, 129.7, 129.4, 128.6, 125.6, 123.5, 123.0, 95.9, 93.8, 90.0, 89.9, 65.5, 31.5, 28.7, 25.7, 22.6, 14.0. MALDI-TOF: Calc. for C₆₉H₆₀O₆: 984.4 (*m*/*z*). Found: 984.8 (*m*/*z*). Found: C, 84.11; H, 6.09. Calc. for C₆₉H₆₀O₆: C, 84.12; H, 6.14.

AEM 8 ¹H NMR (300 MHz, CDCl₃). δ 8.29 (3H, d, J = 1.5 Hz), 8.24 (3H, d, J = 1.5 Hz), 8.02 (3H, dd, J = 8.1, 1.5 Hz), 7.76–7.65 (9H, m), 4.36 (6H, t, J = 6.6 Hz), 4.27 (6H, t, J = 6.6 Hz), 1.78 (12H, m), 1.26 (36H, m), 0.93 (9H, t, J = 6.9 Hz), 0.82 (9H, t, J = 6.9 Hz). ¹³C NMR (50 MHz, CDCl₃): δ 165.2, 134.2, 134.13,134.07, 133.2, 132.7, 131.9, 130.3, 129.2, 129.1, 125.9, 123.3, 123.0, 94.9, 94.2, 92.9, 90.6, 65.8, 65.6, 31.5, 31.4, 29.6, 28.6, 25.6, 22.5, 22.4,14.0, 13.9. FTMS: Calc. for C₉₀H₉₆O₁₂: 1368.7 (*m*/*z*). Found: 1391.7 (M + Na⁺). Found: C, 78.73; H, 7.06. Calc. for C₉₀H₉₆O₁₂: C, 78.92; H, 7.06.

Conclusions

Eight triangle-shaped AEMs of related but different structures were synthesized, and their optical and thermotropic properties were systematically investigated. Four of the studied macrocycles manifested LC phases, which were thoroughly characterized by DSC, POM, and XRD techniques. A number of variants in structure, e.g., the side chain length, side chain linkage, and backbone scaffold, were examined regarding their influence over the thermotropic LC behavior. Size and structure of the mesogen core were important. With three different backbone structures investigated, disparate mesophases were manifested by varied aromatic backbones, showing that core-core interactions among mesogens were decisive for the molecular arrangement and strength of intermolecular interactions. Extension or expansion of the aromatic framework appeared to be favorable for LC phase formation in the investigated systems. The side chain length was found to be one of the pivotal factors as well. Longer dodecvloxy side chains were more conducive to mesophases than shorter hexyloxy chains. Among the macrocycles studied, two molecules having dodecyloxy side chains manifested thermodynamically stable LC phases, while macrocycles having the same mesogen core but tethered with shorter hexyloxy groups did not. Side chain linkage was also critical in governing the mesophase. Two types of side chain linkers were compared. Both macrocycles having ester side chain linkers exhibited LC phases, even when the side chains were the shorter hexyl groups. Of all the macrocycles examined here, a cyclic oligo(phenylene-ethynylene) molecule of C_3 -symmetry having six side chains attached to each of the phenylene units via an ester functionality displayed the most stable LC phase featuring a hexagonal columnar structure.

With a conjugated aromatic backbone, these macrocycles are potentially functional materials. As exemplified in a previously report, they may possess appealing semi-conductive properties.^{23a} Upon further functionalization, *e.g.*, modifying the

backbone structure and/or decorating the interior of the cyclic framework, the molecules may offer more diversified and optimized functions. Their propensity to form LC phases, as demonstrated in the current study, will undoubtedly benefit the material's application and device fabrication. Relevant studies are underway.

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