# Enforced liquid crystalline properties of dibenzo[*a*,*c*]phenazine dimer and self assembly<sup>†</sup>

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Dibenzo[a,c]phenazine dimers with the following features: (i) short spacer, (ii) peripheral chains shorter and longer than the spacers, and (iii) reduced symmetrical structure of the disc were synthesized. The dibenzo[a,c]phenazine disc has enforced the self-assembly of discotic dimers connected through six methylene spacers to form mesophases through a folded conformation in the mesophase. An X-ray diffraction study pinpoints the preferential intra-molecular bridging conformation of these dimers at the mesophase. These new discotic dimers showed polymesomorphism and glass formation. Interestingly, these discotic dimers form organogels with non-polar hydrocarbon solvents and long chain aliphatic alcohols. A superstructure arising from association of the nanofibers was observed with transmission electron microscopy.

## Introduction

Discotic liquid crystalline (DLCs) materials consisting of a disclike rigid aromatic core with several flexible aliphatic side chains that form columnar order assemblies in the mesophase have attracted attention for the past decades due to their promising one-dimension charge and energy migration along their axes. As a consequence, DLCs have become increasingly important for potential applications as functional materials in field effect transistors, photoconductors, light emitting diodes, photovoltaic solar cells, and gas sensors.<sup>1-7</sup> A high degree of long-range order of the DLCs, which is important for the undisturbed onedimension charge migration along the column, has enabled them to compete favorably with single-crystal materials.8 The presence of microscopic local defects at the columnar axis significantly reduced the charge mobility, and therefore the device performance. Hence, a wide range of variation of the core and/or the side chains of the discotic mesogens have been studied to ensure long range ordering at the mesophase and a useful transition temperature for fabrication of devices.5,6,9-11

It has now become apparent that for real applications as active materials in devices, the ease of processing and mechanical robustness of the DLCs have to be taken into consideration. Therefore, recent interest has been centered on the synthesis of novel functionalized dimers, oligomers and polymers with the hope of attaining all the combinations of the properties necessary for DLCs, especially in their ability to form highly ordered anisotropic glasses on cooling down to below the glass transition temperature.<sup>12-17</sup> Dimeric liquid crystalline compounds with two mesogenic units linked together by a flexible spacer that can form

a glassy state have been widely studied mainly because they are an ideal model for higher oligomers and polymers, and also due to their ease in producing a pure product. The relationship between the liquid crystalline behavior and the length and parity of the flexible spacers in dimeric rod-shaped liquid crystalline materials have been widely studied and understood.16,17 However, for the dimeric discotic-family of mesogens, the effect of peripheral substituent and spacer has not been thoroughly investigated and fully understood. Among the most studied dimeric DLCs with a flexible spacer are the triphenylenes18-23 which have been recently reviewed<sup>24</sup> together with other dimers based on benzene,<sup>25,26</sup> phthalocyanine,<sup>27</sup> cyclotetraveratrylene<sup>28</sup> and hexabenzocoronenes.<sup>29</sup> In all the discotic dimers reported, the spacer lengths are long and must be equal to or longer than the peripheral side chains to show mesomorphism, a property closely related to the ease of reorientation between the discogens in neighboring columns with intercalated arrangement. The mesophases for these dimeric discotic liquid crystals have generally been discussed in the context of the discogens being arranged in an inter-columnar manner<sup>19,24,25</sup> with the two subunits of the dimer residing in neighboring columns (nonintercalated or intercalated), although the possibility of an intramolecular bridging with the two subunits residing in the same column cannot be ruled out.20

The various possible stacking arrangements for the discotic dimers are shown in Fig. 1. But, unlike the calamatic dimers whereby the terminal chain can be longer than the spacer to give a non-intercalated arrangement in the mesophase, such a system has not been reported for the discotic dimers. For such unprecedented discotic dimers to show mesomorphism, we envisage that this will involve mainly an intramolecular arrangement between the core–core interactions which is unknown to date. Substituted dibenzo[a,c]phenazine has been reported to enhance stabilised columnar structure through an antiparallel packing of the core and is a candidate of choice for this study.<sup>30,31a,b</sup> In the present work, we hope to apply this property of the mesogenic dibenzo[a,c]phenazine and extend the study to unconventional discotic dimers containing peripheral chains longer than the

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Intercolumnar Stacking

Fig. 1 Possible stacking of discotic dimers into columnar structures at the mesophase.



Scheme 1 The synthesis of dibenzo[a,c]phenazine dimers DiQXs and DiHDBPs.

spacer, and specifically with a much shorter spacer than reported, with the hope of creating novel liquid-crystalline materials. Interestingly, when four alkoxy peripheral chains are longer than the spacer, this will at the same time create reduced symmetry in each unit, an advantage for the formation of Col glasses. Such a system has never been synthesized and this report will provide an insight for the first time. We now report on the synthesis of this new series of compounds which were found to exhibit mesomorphism as determined by polarized optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The anticipated advantage of having a reduced symmetry in each unit of the dimer was found to give Col glass.

## **Results and discussion**

#### Synthesis

The synthetic strategy of the discotic dimers makes use of the monoalkylated catechol<sup>31</sup> as starting material and is outlined in

Scheme 1. Also, we envisioned that it will be more appropriate to introduce the flexible methylene spacer of the desired discotic dimers at an early stage through the bis-alkylation of the mono-alkylated catechol. The versatile intermediate 2 can be readily prepared from the reaction of monoalkylated catechol with the appropriate dibromoalkane in good yield. A two steps nitration of 2 gave the tetra-nitration product 3 in good yield; and is subsequently reduced to the tetra-amine 4. The target dimeric discotic compounds, **DiQXs** and **DiHDBPs**, are readily accessible by the straightforward condensation of 4 with 1,2-diketone derivatives 5 and 6, respectively. The large structural differences between the reactants and products at every stages of the synthesis had enabled us to readily obtain **DiQXs** and **DiHDBPs** in high purity.

#### Liquid crystalline properties (POM, DSC and XRD)

The phase-forming properties of bisquinoxaline **DiQX(6,6,6)** and **DiQX(6,6,12)** were found to be non-mesogenic, melting directly

from the crystalline solid to an isotropic liquid. The nonplanarity of the unfused aromatic ring precluded the mesophase formation.

The new **DiHDBP(6,6,6)** with six methylene groups as the spacer was found to be liquid crystalline under a polarized optical microscope (POM) (Fig. 2a, c). This constitutes a dimeric

discotic system possessing the shortest spacer with mesogenic properties known to date. Even more intriguing, **DiHDBP(6,6,8)** with the peripheral side chains longer than the spacer length was also found to be mesogenic under POM. The transition temperatures and enthalpies of these two compounds measured by DSC are summarized in Table 1. The XRD profile for



**Fig. 2** Left: liquid crystalline properties of **DiHDBP(6,6,6)** (a) polarized optical micrograph of  $Col_h$  mesophase at 115 °C, ×200, with cover glass in cooling process (black region = homeotropic); (b) the corresponding powder X-ray diffractogram of  $Col_h$ ; (c) polarized optical micrograph of the  $Col_r$  phase at room temperature, ×200, with cover glass in cooling process; (d) the corresponding powder X-ray diffractogram of  $Col_r$ . Right: Graphical representation for the intercolumnar distance and mesophases as the peripheral length increases.

Compound	Phase transition	Range of columnar phase/°C	Persistent time of supercooling Col phase
DiQX(6,6,6)	$K = \frac{15.5 (20.63)}{5.4 (-30.00)} K_1 = \frac{74.2 (7.81)}{5.4 (-30.00)} = 1$		
DiQX(6,6,12)	$K = \frac{\frac{26.7 (76.85)}{22.3 (-52.27)}}{K_1} \frac{K_1}{82.0 (15.13)} = 1$		
DiHDBP(6,6,6)	$ \begin{array}{c} \text{Col}_{\text{ro}} & \underbrace{53.7 \ ^{\text{o}}\text{C} \ (6.08)}_{43.3 \ ^{\text{o}}\text{C} \ (-8.70)} & \text{Col}_{\text{ho}}^{-1} \underbrace{\frac{127.4 \ ^{\text{o}}\text{C} \ (6.35)}_{152.9 \ ^{\text{o}}\text{C} \ (-9.35)} & \text{Col}_{\text{ho}}^{-2} \underbrace{158.2 \ ^{\text{o}}\text{C} \ (8.11)}_{152.9 \ ^{\text{o}}\text{C} \ (-9.35)} & \text{I} \end{array} \right. $	109.6	several hours
DiHDBP(6,6,8)	$Col_{ro} \xrightarrow{54.6 (5.97)}{42.8 (-1.91)} Col_{ho} \xrightarrow{134.2 (7.56)}{130.8 (-7.47)} I$	79.6 88.0	several hours
DiHDBP(6,6,10)	G <u>49.1 (-27.33)</u> Col <sub>ho</sub> <u>87.0 (49.96)</u> <u>84.9 (-5.31)</u> I		several hours
DiHDBP(6,6,12)	G 73.9 (95.58) 20.8 (-124.82) Col <sub>ho</sub> 75.8 (-4.54)	55.0	several hours
DiHDBP(6,10,6)	$Col_{ro} \xrightarrow{52.5 \text{ °C (1.11)}}_{47.6 \text{ °C (-0.96)}} Col_{ho} \xrightarrow{180.5 \text{ °C (12.92)}}_{175.0 \text{ °C (-12.88)}} I$	128.0 127.4	4 months $>$ T $>$ 1 month
DiHDBP(6,12,6)	$Col_{ro} = \frac{47.5 \ ^{\circ}C \ (3.48)}{43.8 \ ^{\circ}C \ (-1.70)} Col_{ho} = \frac{173.5 \ ^{\circ}C \ (8.75)}{169.5 \ ^{\circ}C \ (-8.30)} I$	126.0 125.7	>4 months

**Table 1** The phase behaviors of **DiQX**s and **DiHDBP**s. The transition temperatures (°C) and enthalpies (in parentheses/kJ mol<sup>-1</sup>) were determined by DSC at 10 °C min<sup>-1.<sup>a</sup></sup>

<sup>*a*</sup> K, crystalline phase; Col<sub>h</sub>, hexagonal columnar mesophase; I, isotropic phase; G, glassy state. Persistent time of supercooling Col phase: the time needed for supercooled Col phase to return to crystalline at room temperature.

DiHDBP(6,6,6) in Fig. 2 showed at the small angle region one very sharp strong reflection indexed as (100) and the second weak reflection indexed as (110) with a reciprocal spacing ratio of 1:( $\sqrt{3}$ ) for a Col<sub>b</sub> lattice at high temperature; and on cooling the reflection indexed at (100) splits into two reflections corresponding to the Miller indices of (110) and (200) for a Col<sub>r</sub> lattice. The texture from POM at these temperatures also showed the change from Col<sub>b</sub> to Col<sub>r</sub> phase. The number of molecules in an ab\*c unit is generally calculated to be 2 for a rectangular lattice based on the formula<sup>32</sup>  $Z = (\rho \{(abc)^* 10^{-24}\}N)/M$ , whereby  $\rho$  is the density, a and b are the lattice constants of the rectangular mesophase (A), c is the mean stacking distance within the column (Å), M is the molecular weight and N is Avogadro's number. However, the number of molecules (Z) in the rectangular unit cell for DiHDBP(6,6,6) and DiHDBP(6,6,8) were calculated to be around 1 when the density was assumed to be 1 g cm<sup>-3</sup>. This implies that their mesophases have a rectangular lattice with a Col<sub>r</sub> (P2m) symmetry.<sup>32,33</sup> Calculation of the molecular length



Fig. 3 The transformation from hexagonal to rectangular packing.

Table 2 Variable-temparature XRD data for DiHDBPs

of fully extended DiHDBP(6,6,6) (extrapolating from the structure) gave 46.46 Å, much larger than that observed in the XRD with an intercolumnar distance of 31.74 Å. This discrepancy becomes more obvious later with longer spacer length. This observation, together with the ease of complete reorientation, indicates the subunits of the dimer are residing in the same column (intramolecular). The P6mm hexagonal phase transformation to the P2m rectangular phase is illustrated in Fig. 3. At first, on cooling down, the side chains became more rigid, leading to the slight expansion of the hexagonal b parameter (Fig. 3b). The final transformation of the hexagonal phase to the P2m rectangle phase can be envisioned as the gliding of the central columns vertically (Fig. 3c), this time causing further expansion laterally between the columns. This is in line with the a' and b' parameters of the P2m rectangle observed for the XRD (Table 2). Thus, for DiHDBP(6,6,6) and DiHDBP(6,6,8), the columns can slide freely and randomly reorientate about the columnar axes. Our dibenzo[a,c]phenazine is the first dimeric system with a short spacer to show mesomorphism reported to date. Although Boden<sup>21</sup> had implied that dimeric discotics with a short spacer can have low strain bridging only in an intramolecular manner (intra-1,2 and intra-1,3), no such short spacer has been shown to be liquid crystalline. Furthermore, since packing of the dimer can be inter-molecular and intra-molecular (Fig. 1) one will expect a greater ease of the intra-molecular packing to undergo reorientation. As such, it appears that the dimer adopts a folded conformation in the liquid crystalline state. Furthermore, a simplified Universal Force Field calculation<sup>34a,b</sup> of the unsubstituted **DiHDBP**-dimer shows that the

Compound	Mesophase	Lattice constant/Å	Obsd (calcd) spacing/Å	Miller indices	Halos obsd/Å	Number of Molecule in Col <sub>r</sub> (Z)
DiHDBP(6,6,6)	$Col_{ho}$ at 120 $^{\circ}C$	<i>a</i> = 21.52	18.64 10.71	(100) (110)/(003)	4.64, 3.56	
	$\text{Col}_{\text{ro}}$ at 30 $^{\circ}\text{C}$	a = 31.74, b = 24.31	19.30	(110) (110) (200)	4.46, 3.58	Z = 0.99
DiHDBP(6,6,8)	$Col_{ho}$ at 85 $^{\circ}C$	<i>a</i> = 22.92	19.85 11.46	(200) (100) (110) (200)	4.56, 3.58	
	Col <sub>ro</sub> at 30 °C	a = 33.60, b = 26.65	20.88 16.80 10.55	(200) (110) (200) (310)/(003)	4.42, 3.52	Z = 1.00
DiHDBP(6,6,10)	$Col_{ho}$ at 50 $^{\circ}C$	<i>a</i> = 24.79	7.49 21.47 12.37	(420) (100) (110)	4.50, 3.54	
DiHDBP(6,6,12)	$Col_{ho}$ at 50 $^{\circ}C$	<i>a</i> = 25.43	22.02 8.13	(110) (100) (210) (003)	4.54, 3.55	
DiHDBP(6,10,6)	$Col_{ho}$ at 120 $^{\circ}C$	<i>a</i> = 21.63	10.76 18.73 10.82	(100) (100)/(003) (210)/(002)	4.54, 3.50	
	$Col_{ro}$ at 30 $^{\circ}C$	a = 33.90, b = 22.80	18.92 16.95 10.55	(210)/(002) (110) (200) (300)/(003)	4.42, 3.55	Z = 0.95
DiHDBP(6,12,6)	$Col_{ho}$ at 120 $^{\circ}C$	<i>a</i> = 21.99	8.44 19.04 11.00 9.61	(400) (100) (110) (200)	4.60, 3.50	
	$Col_{ro}$ at 30 $^{\circ}C$	a = 34.44, b = 23.06	7.18 19.16 17.22	(210)/(002) (110) (200)	4.50, 3.53	Z = 0.96



**Fig. 4** The possible structures by the force field calculations viewed from the side (without the methoxy groups for clarity).

extended (all-*trans*) conformation **A** is less favourable than the folded conformation **B** (calculated to be about 20 Kcal mol<sup>-1</sup>) (Fig. 4). The ability of **DiHDBP(6,6,6)** to reorientate readily from  $Col_h$  to  $Col_r$  can be taken as an indication of the two subunits of the dimer residing in the same column (intra-molecular packing of the folded conformation), and in agreement with our modeling results.

Although our data indicates the intra-molecular packing of the dimeric discotic system at the mesophase, at this point we cannot totally rule out the possibility of the inter-molecular participation. We hope to prove the true nature of the intra-molecular stacking by synthesizing DiHDBP(6,6,10) and DiHDBP(6,6,12) which have an increased length of the tetraalkoxy peripheral side chains (R), while maintaining the length of the short spacer (-O(CH<sub>2</sub>)<sub>6</sub>O-) and the internal chain. The extremely long tetraalkoxy peripheral chains in the dimeric discotic molecules must surely forbid the individual discs from aligning on top of each other within a column in the intermolecular stacking manner. If these dimeric compounds showed mesomorphism, this must be derived solely from an intra-molecular stacking into ordered columns. More importantly, the individual discs in this dimer also becomes less symmetrical, whereby introducing an extra degree of disorder that can favor the glassy phase at room temperature. DiHDBP(6,6,10), with a four methylene group longer spacer, was also found to be liquid crystalline under POM. DiHDBP(6,6,10) shows an exothermic transition (second heating run) typically seen during supercooling for a glass to crystalline transition before melting into the LC phase, while the second endothermic transition suggests isotropization as seen in the DSC (see Fig. S1b, in ESI<sup>†</sup>). The high enthalpy for isotopization for longer side chains suggests an increasing van der Waals interactions of the longer side chains between the subunits for the dimeric unit within the respective column. On cooling, however,

no crystallization was detected by DSC and XRD, revealing the formation of Col<sub>b</sub> glassy phase. Surprisingly, DiHDBP(6,6,12), whereby the peripheral tetraalkoxy chain is twice the spacer length was also found to be mesogenic. The increasing peripheral chain length in DiHDBP(6,6,12) further increases the enthalpies of the phase transitions (second heating), a property mainly observed for main-chain discotic polymers, whereby accounting for their Col<sub>b</sub> glass phase. It is likely that the intra-molecular stacked columns can be further interlinked by their side-groups through enhanced interdigitalization. Thus DiHDBP(6,6,10) and DiHDBP(6,6,12) mesogenic properties behave rather similar to that of the polymers.<sup>35</sup> The influence of increasing the length of the side-chains on the intracolumnar distance and mesogenic temperature is summarized in Fig. 2. It can be clearly seen that as the side-chain length increases the intercolumnar distance also increases, and there is a lowering of the melting  $(T_{K-Col})$  and clearing temperature ( $T_{\text{Col-I}}$ ).

The most significant proof of intracolumnar stacking of the dimers in the columnar phase comes from the lengthening of the spacer in DiHDBP(6,10,6) and DiHDBP(6,12,6). We postulated that the lengthening of the spacer length will lead to different observations in their XRD at the mesophase for the different packing: (i) unchanged intercolumnar distance for intra-molecular stacking, and (ii) lengthening of the intercolumnar distance for inter-molecular stacking. Analysis of the X-ray diffraction data for the Col<sub>h</sub> phase of **DiHDBP(6,10,6)** and **DiHDBP(6,12,6)** clearly showed that their intercolumar distances remain fairly constant at around 21.63-21.99 Å, irrespective of the spacer length (see Fig. S2<sup>†</sup>). Their intercolumnar distances are very similar to that found for DiHDBP(6,6,6). We have thus further substantiated that the discs adopted solely an intracolumnar stacking conformation for DiHDBPs. Transition from Col<sub>h</sub> to the Col<sub>r</sub> phase on cooling was again observed for DiHDBP(6,10,6) and DiHDBP(6,12,6), driven by a reduction in chain mobility.

The intercolumnar distance *a* from the XRD is much shorter than that of a fully extended dimer, again implying intramolecular packing. However a slight shortening in the rectangular length parameters as calculated by  $\sqrt{3} \times a$  from the hexagon, and broadening of the rectangular width was observed, accounted for the reduction in chain mobility whereby at the molecular level this could result in a slightly different spatial profile. At room temperature, these form glassy phases that can

Solvent	Solubility and critical gelation concentration						
	DiHDBP(6,6,8)	DiHDBP(6,6,10)	DiHDBP(6,12,6)	Monomer 6	Monomer 12		
Hexane	$16 \text{ mg mL}^{-1}$	$10 \text{ mg mL}^{-1}$	Insoluble	Soluble	Soluble		
1-Octanol	$18 \text{ mg mL}^{-1}$	$12 \text{ mg mL}^{-1}$	Insoluble	$38 \text{ mg mL}^{-1}$	$10 \text{ mg mL}^{-1}$		
Cyclohexane	$25 \text{ mg mL}^{-1}$	$13 \text{ mg mL}^{-1}$	Soluble	Soluble	Soluble		
Ethyl acetate	$38 \text{ mg mL}^{-1}$	Insoluble	Insoluble	$55 \text{ mg mL}^{-1}$	25 mg mL <sup>-1</sup>		
Ethanol	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble		
Acetone	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble		
Dimthylformamide	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble		
Acetonitrile	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble		
Dichloromethane	Soluble	Soluble	Soluble	Soluble	Soluble		
Tetrahydrofuran	Soluble	Soluble	Soluble	Soluble	Soluble		
Toluene	Soluble	Soluble	Soluble	Soluble	Soluble		

 Table 3
 Gelation behaviors of dimer and monomer in different organic solvents

be stable for months. Another interesting observation is the increase of isotropic temperatures from **DiHDBP(6,6,6)** to **DiHDBP(6,10,6)**. These observations led to the conclusion that the dimeric discotic molecules form folded conformations predominantly, resulting in the exclusive formation of intracolumnar stacking within the column, a result extremely different from the previously reported dimers.

## Gel formation

Eleven solvents consisting of hydrocarbon solvents, alkyl alcohols, and polar solvents were used to test the gelation ability of the dimers synthesized. The dimer DiHDBP(6,6,8) was found to form gels with hexane, cyclohexane, 1-octanol and ethyl acetate. The dominant forces responsible for DiHDBP(6.6.8) to form a gel include; intra-molecular stacking,  $\pi - \pi$  interactions, dipoledipole interaction, and van der Waals forces. Furthermore, the lengthening of the peripheral alkyl chains in DiHDBP(6.6.10) favors gel formation, probably through a better interdigitalization between the alkyl groups of the columns which formed complex 3D intertwining networks. The critical concentrations required for gel formation are summarized in Table 3. These organogels formed are thermo-reversible and show a luminescent property under a UV lamp. The lengthening of the spacer, as in DiHDBP(6,12,6), did not promote gel formation. We have previously synthesized the monomeric dibenzo[a,c]phenazine with hexahexyloxy side-chains (Monomer 6) and hexadocecyloxy side-chains (Monomer 12).<sup>31</sup> It was found that the dibenzo[a,c]phenazine monomers only form gels in hydrogen bonding (1octanol) and polar solvent (ethyl acetate).

We next used scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to examine the mesoand nanoscale structures of the xerogels (Fig. 5). The SEM image of the xerogel prepared from hexane solution (16 mg mL<sup>-1</sup>) and onto a silicon wafer substrate shows irregular fibrous selfassembled morphology. TEM measurements were further



Fig. 5 Gel behavior of DiHDBP(6,6,8); (a) SEM images of xerogel prepared from hexane solution (16 mg mL<sup>-1</sup>) onto the silicon wafer substrate, (b) TEM image was obtained from hexane solution ( $1 \times 10^{-5}$  M) aged for 18 h and drop-cast onto a copper grid, (c) expanded TEM images, (d) electron diffraction pattern from a single fiber, (e) photograph of gel under natural light, (f) photograph of gel under UV lamp (excited with 365 nm light).

carried out to investigate the nature of the fiber. The TEM thin film was prepared from  $1 \times 10^{-5}$  M hexane solution aged for 18 h and drop-cast onto the copper grid. The TEM image clearly showed one-dimensional association of the nanofibers. The diffractogram shows that there was no repeating units in the associated fibers.

### **Photophysical properties**

Fig. 6 shows the UV-vis absorption and fluorescence spectra of **DiHDBP(6,6,6)** and **DiHDBP(6,10,6)** in  $10^{-5}$  M CH<sub>2</sub>Cl<sub>2</sub> solution. The spectra in solution showed similar UV-vis absorption at similar wavelengths at 284 nm for the discotic dimers **DiHDBP(6,6,6)** and **DiHDBP(6,10,6)**. The UV-vis absorption of **Monomer 6** (hexahexyloxydibenzo-[*a*,*c*]phenazine) was also recorded and shows a similar trend.

The fluorescence spectra for all these compounds upon excitation at 284 nm shows nearly identical emission peaks at around 544 nm. Thus, photophysical data might suggest that they are not folded in the  $10^{-5}$  M solution.

#### **Electrochemical properties**

The cyclic voltametry (CV) measurements of DiHDBP(6,6,6) was performed in dichoromethane for the anodic and tetrahydrofuran for the cathodic scan containing 0.05 M tetrabutylammonium perchlorate as the supporting electrolyte and a scan rate of 50 mV s<sup>-1</sup>. Platinum wire was used as the counter and working electrode with Ag/Ag<sup>+</sup> (0.01M AgNO<sub>3</sub>) as the reference electrode, and ferrocene used as the internal standard. Fig. 7 shows DiHDBP(6,6,6) possesses two quasi-reversible oxidation half-wave potentials  $(E_{1/2})$  at 0.95 and 1.08 V. Also, two reversible reduction half-wave potentials at -1.48 V and -1.92 V were observed. DiHDBP(6,6,6) has the dual ability of donating and accepting electrons at the disc. The Monomer 6 (hexahexyloxydibenzo-[a,c]phenazine) was found to possess an oxidation halfwave potential at 1.04 V, and two reduction half-wave potentials at -1.69 V and -2.09 V were observed. Ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple was used as an internal standard for all the CV measurements. The corresonding HOMO/LUMO can be



Fig. 6 Normalized UV–vis absorption and fluorescence emission spectrum of **DiHDBP(6,6,6)**, **DiHDBP(6,10,6)** and **Monomer 6**. The fluorescence spectrum was obtained upon excitation at 284nm (at 298 K, in  $10^{-5}$  M CH<sub>2</sub>Cl<sub>2</sub> solution).





Fig. 7 Cyclic voltammogram and differential pulse-voltammetry diagrams of Monomer 6 (top line) and DiHDBP(6,6,6) ( $10^{-3}$ M) (bottom line) in TBAPF<sub>6</sub> ( $0.05 \text{ mol } L^{-1}$ ) solutions in degassed anhydrous solvent. The reductions were recorded in THF and the oxidations in CH<sub>2</sub>Cl<sub>2</sub>, using Ag/AgNO<sub>3</sub> standard electrode. (Scan rate: 50 mV s<sup>-1</sup>).

further derived using the first oxidation and reduction wave, using the following equation: HOMO/LUMO =  $-4.8 - E_{ox}/E_{red}$ whereby  $E_{ox}/E_{red}$  is the onset potential of the first oxidation or reduction wave *versus* Fc/Fc<sup>+</sup>. The HOMO and LUMO energy level for **DiHBDP(6,6,6)** was estimated to be -5.23 eV and -2.93eV, respectively. Interestingly, the HOMO energy of **Monomer 6**, (-5.36 eV) is lower than **DiHBDP(6,6,6)**, while the LUMO energy of **Monomer 6** (-2.73 eV) is higher than **DiHBDP(6,6,6)**. This indicates that there is a slight increase in the interaction between the individual discotic core for the dimer in the  $10^{-3}$  M solution. This is indicative of a folded conformation of the dimer at this concentration.

#### Conclusion

In summary, we have presented a new family of discotic liquid crystal dimers, **DiHDBP**s based on dibenzo[a,c]phenazine that preferentially form into a folded conformation. From the XRD studies, it is reasonable to assume these mesogens adopt the folded conformation in the liquid crystalline state. This has enabled liquid crystalline formation for the shortest spacer known to date. In the columnar phase, the dimeric molecules stack predominantly in an intra-columnar manner to form columns. As such, peripheral side chains longer than the spacer can also be liquid crystalline. A rich polymesomorphism from Col<sub>h</sub> to Col<sub>r</sub> was also observed and they form glasses on cooling to room temperature that can last for a few hours to months. Interestingly, they also form organogels, indicating the great ability of DiHDBPs to form a 3-D network. These findings may contribute to the development of polymer like stable ordered self-assembly materials important for future applications in devices.

#### **Experimental section**

#### Materials and methods

All reactions were conducted under an atmosphere of nitrogen in oven-dried glassware. Dichloromethane was distilled over

calcium hydride. Nuclear magnetic resonance spectra were recorded on a Varian Unity-INOVA-500 MHz spectrometer using CDCl<sub>3</sub> as solvent. Chemical shifts are reported in ppm relative to residual CDCl<sub>3</sub> ( $\delta = 7.26$ , <sup>1</sup>H; 77.0, <sup>13</sup>C). Mass spectra were obtained on FT-MS on Bruker APEX II or MALDI-TOF on Bruker Autoflex III TOF/TOF. Elemental analyses were carried out on Heraeus CHN-O Rapid Elementary Analyzer and Elementar vario EL III. Differential scanning calorimetry (DSC) was measured on a Perkin-Elmer Pyris 1 with heating and cooling rates of 10 °C min<sup>-1</sup>. Polarized optical microscopy (POM) was carried out on a OLYMPUS CX41 with a Mettler FP90/FP82HT hot stage system. X-Ray powder diffraction (XRD) data were collected on the wiggler beamline BL17A of the National Synchrotron Radiation Research Center (NSRRC), Taiwan, using a triangular bent Si (111) monochromator and a wavelength of 1.33367 Å. The sample in a 1 mm capillary was mounted on the Huber 5020 diffractometer. An air stream heater is equipped at BL17A beamline and the temperature controller is programmable by a PC with a PID feed back system. UV-vis spectra were obtained on an HP 8453 diode-array spectrophotometer. Photoluminescence (PL) spectra were measured using a Hitachi F-4500 luminescence spectrometer. Cyclic voltammetry (CV) measurements were undertaken on a BAS 100 B/W electrochemical analyzer. Scanning electron microscopy (SEM) was carried out by using the JSM-6701F, Field Emission Scanning Electron in National University of Singapore. Transmission electron microscopy (TEM) was carried out by using the JEM-2100F, Field Emission Electron Microscopy at 200 keV in Nanyang Technological University in Singapore.

#### Synthesis of compounds

2-Hexyloxyphenol 1, 3,3',4,4'-tetrakisalkoxybenzil 5, and 2,3,6,7-tetrakis(alkoxy)phenanthrene-9,10-dione 6 were synthesized according to literature procedures.<sup>36,37</sup>

**1,x-Bis(2-alkoxyphenoxyl)alkane (2).** In a two-neck roundbottom flask (100 mL) fitted with a condenser with a nitrogen inlet containing ethanol (50 mL) were added 2-hexyloxyphenol (1 equivalent) and potassium carbonate (2.5 equivalent) and the mixture stirred at room temperature for 1 h. After this time, the dibromoalkane (1.1 equivalents) was added, and the reaction mixture was refluxed for one day. The solid residue from the reaction mixture was filtered, and the filtrate was evaporated to dryness. The crude product was then dissolved in dichloromethane and the dichloromethane layer washed with water and brine. The solvent was dried over MgSO<sub>4</sub> and evaporated. The crude product was further purified by column chromatography on silica gel (hexane–ethyl acetate 15 : 1 as eluent) or recrystallized from 1 : 1 dichloromethane–methanol. The yield of **2a** is 91%, **2b** is 93%, and **2c** is 89%.

**2a**: Mp: 72 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  6.89 (s, 8H), 4.03–3.98 (m, 8H), 1.87–1.79 (m, 8H), 1.59–1.55 (m, 4H), 1.50–1.44 (m, 4H), 1.37–1.32 (m, 8H), 0.92–0.89 (m, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  149.21, 149.13, 121.05, 120.96, 114.11, 114.02, 69.21, 69.11, 31.58, 29.30, 29.26, 25.85, 25.68, 22.61, 14.02. Mass (EI): *m*/*z* 470 [M<sup>+</sup>]. Anal. calcd for C<sub>30</sub>H<sub>46</sub>O<sub>4</sub>: C, 76.55; H, 9.85. Found: C, 76.30; H, 9.78.

**2b**: Mp: 68 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  6.89 (s, 8H), 4.00 (t, J = 6.5 Hz, 8H), 1.84–1.79 (m, 8H), 1.51–1.44 (m, 8H), 1.37–1.33(m, 16H), 0.92–0.89 (m, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  149.21, 120.98, 114.08, 114.07, 69.20, 69.10, 31.61, 29.57, 29.43, 29.34, 29.29, 26.04, 25.71, 22.62, 14.03. Mass (EI): m/z 526 [M<sup>+</sup>]. Anal. calcd for C<sub>34</sub>H<sub>54</sub>O<sub>4</sub>: C, 77.52; H, 10.33. Found: C, 77.12; H, 10.21.

**2c**: Mp: 51 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  6.88 (s, 8H), 4.00–3.98 (m, 8H), 1.84–1.78 (m, 8H), 1.49–1.43 (m, 8H), 1.36–1.28 (m, 20H), 0.93–0.89 (m, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  149.21, 120.98, 114.08, 69.25, 31.61, 29.62, 29.44, 29.33, 29.29, 26.04, 25.71, 22.62, 14.03. LRMS (ESI): *m*/*z* 577 [M + Na<sup>+</sup>]; HRMS (ESI) *m*/*z* 577.4236 [M + Na<sup>+</sup>] (577.4233 calculated for C<sub>36</sub>H<sub>58</sub>NaO<sub>4</sub> [M + Na<sup>+</sup>]).

**1,x-Bis(2-alkoxy-4,5-dinitro-phenoxyl)alkane (3).** To a two neck round-bottom flask containing dichloromethane (50 mL), acetic acid (50 mL), and compound **2** (2 g) cooled to 0 °C was added slowly 65% nitric acid (6 mL). The reaction was allowed to warm to room temperature and stirred for a further 1 h. The mixture was again cooled to 0 °C, 100% nitric acid (3 mL) was added slowly, the mixture was allowed to warm to room temperature and stirred overnight. After completion of the reaction, the reaction mixture was poured into ice–water. The yellow precipitate was collected by filtration and washed with ice–water to remove the residual acid. The yield of **3a** is 66%, **3b** is 68%, and **3c** is 65%.

**3a**: Mp: 153 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.30 (d, J = 5 Hz, 4H), 4.14–4.09 (m, 8H), 1.94–1.85 (m, 8H), 1.59–1.25 (m, 16H), 0.92–0.89 (m, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  151.77, 151.52, 136.64, 136.34, 107.85, 107.82, 70.17, 69.81, 31.32, 28.60, 25.45, 25.42, 22.50, 13.94. Mass (FAB): 650 [M<sup>+</sup>]. Anal. calcd for C<sub>30</sub>H<sub>42</sub>N<sub>4</sub>O<sub>12</sub>: C, 55.38; H, 6.51; N, 8.61. Found: C, 55.21; H, 6.55; N, 8.56.

**3b**: Mp: 134 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.30 (s, 4H), 4.10 (t, J = 6.5 Hz, 8H), 1.89–1.86 (m, 8H), 1.59–1.26 (m, 24H), 0.93–0.90 (m, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  151.76, 151.70, 136.50, 136.43, 107.86, 107.85, 70.17, 70.12, 31.35, 29.68, 29.45, 29.23, 28.68, 28.62, 25.78, 25.45, 22.51, 13.95. Mass (FAB): m/z 706 [M<sup>+</sup>]. Anal. calcd for C<sub>34</sub>H<sub>50</sub>N<sub>4</sub>O<sub>12</sub>: C, 57.78; H, 7.13; N, 7.93. Found: C, 57.48; H, 7.22; N, 7.83.

**3c**: Mp: 135 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.29 (s, 4H), 4.10 (t, J = 6.5 Hz, 8H), 1.89–1.84 (m, 8H), 1.58–1.30 (m, 28H), 0.93–0.90 (m, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  151.76, 151.72, 136.44, 107.86, 70.17, 70.15, 31.35, 29.56, 29.53, 29.24, 28.67, 28.62, 25.79, 25.45, 22.51, 13.95. LRMS (ESI): m/z 757 [M + Na<sup>+</sup>]; HRMS (ESI) m/z 757.3632 [M + Na<sup>+</sup>] (757.3636 calculated for C<sub>36</sub>H<sub>54</sub>N<sub>4</sub>NaO<sub>12</sub> [M + Na<sup>+</sup>]).

**1,x-Bis(2-alkoxy-4,5-diamino-phenoxyl)** (4). In a two-neck flask containing dinitro compound **3** (1 equivalent) and 10% Pd on carbon (0.1 g) in ethanol (35 mL) was added hydrazine monohydrate (10 equivalent) slowly, and the reaction mixture was refluxed for 2 days under nitrogen. The reaction solution was filtered and the filtrate was evaporated under vacuum. The diamine is unstable and had to be used *in situ*.

1,x-Bis (2,3,6,7-tetrakis(alkoxy)-12-(hexyloxy)dibenzo[*a*,*c*]-phe nazin-11-yloxy)alkane (DiHDBPs) and 1,6-bis(2,3-bis(3,4-

**bis(alkoxy)phenyl)-7-(hexyloxy)quinoxalin-6-yloxy)-hexane.** To a solution of the corresponding amine **4** and benzyl **5** or **6** in dichloromethane (50 mL) was added acetic acid (1 mL). The reaction mixture was stirred under nitrogen for 24 h. Removal of the solvent *in vacuo* yielded a crude product that was rigorously purified by chromatographic separation on silica gel using ethyl acetate–*n*-hexane 1 : 5 as eluent and recrystallized from acetone or ethanol–dichloromethane. The yield of **DiQX(6,6,6)** is 34%, **DiQX(6,6,12)** is 30%, **DiHDBP(6,6,6)** is 30%, **DiHDBP(6,6,12)** is 33%, **DiHDBP(6,10,6)** is 28% and **DiHDBP(6,12,6)** is 26%.

**DiQX(6,6,6)**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.40 (s, 2H), 7.39 (s, 2H), 7.07 (d, J = 8.5 Hz, 4H), 7.00 (s, 4H), 6.82 (d, J = 8.5 Hz, 4H), 4.21 (t, J = 6.5 Hz, 4H), 4.17 (t, J = 6.5 Hz, 4H), 3.99 (t, J = 6.5 Hz, 8H), 3.80 (t, J = 6.5 Hz, 8H), 2.03–1.66 (m, 24H), 1.52–1.25 (m, 64H), 0.91–0.88 (m, 30H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  152.34, 152.30, 150.36, 150.34, 149.23, 148.53, 148.52, 137.90, 137.86, 132.20, 122.46, 115.20, 113.17, 107.15, 69.07, 69.02, 68.96, 68.81, 31.53, 31.46, 31.42, 29.10, 28.99, 28.75, 28.68, 25.78, 25.58, 25.58, 25.56, 22.53, 22.52, 22.50, 13.93. Mass (MALDI-TOF): *m*/*z* 1680.347 [M + H<sup>+</sup>]. Anal. calcd for C<sub>106</sub>H<sub>158</sub>N<sub>4</sub>O<sub>12</sub>: C, 75.76; H, 9.48; N, 3.33. Found: C, 75.61; H, 9.15; N, 3.05.

**DiQX(6,6,12)**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.41 (bs, 4H), 7.09–7.06 (m, 4H), 6.99 (d, J = 8.5 Hz, 4H), 6.83 (d, J = 8.5 Hz, 4H), 4.23–4.16 (m, 8H), 3.99 (t, J = 6.5 Hz, 8H), 3.82–3.78 (m, 8H), 2.00–1.63 (m, 24H), 1.55–1.26 (m, 160H), 0.94–0.87 (m, 30H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  152.50, 150.36, 149.39, 148.62, 148.60, 137.84, 132.16, 122.59, 115.30, 113.27, 107.11, 69.19, 69.09, 68.96, 31.92, 31.54, 31.50, 29.74, 29.70, 29.68, 29.66, 29.64, 29.47, 29.43, 29.38, 29.36, 29.24, 29.13, 28.85, 28.75, 26.02, 25.90, 25.67, 25.63, 22.68, 22.57, 14.10, 14.00. Mass (MALDI-TOF): *m*/*z* 2354.133 [M + H<sup>+</sup>]. Anal. calcd for C<sub>154</sub>H<sub>254</sub>N<sub>4</sub>O<sub>12</sub>: C, 78.59; H, 10.88; N, 2.38. Found: C, 78.49; H, 10.95; N, 2.40.

**DiHDBP(6,6,6):** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.74 (s, 2H), 8.69 (s, 2H), 7.73 (s, 4H), 7.53 (s, 2H), 7.50 (s, 2H), 4.35–4.24 (m, 24H), 2.06–1.94 (m, 24H), 1.73–1.38 (m, 64H), 0.97–0.92 (m, 30H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  152.65, 150.97, 150.94, 149.24, 139.27, 138.91, 125.65, 125.60, 123.96, 107.92, 107.86, 106.63, 106.31, 69.56, 69.08, 69.01, 68.96, 68.71, 31.77, 31.68, 31.54, 29.35, 29.30, 28.93, 28.89, 25.83, 25.80, 25.73, 25.64, 22.63, 22.61, 14.03, 14.01. Mass (MALDI-TOF): *m/z* 1676.090 [M + H<sup>+</sup>]. Anal. calcd for C<sub>106</sub>H<sub>154</sub>N<sub>4</sub>O<sub>12</sub> : C, 75.95; H, 9.26; N, 3.34. Found: C, 75.70; H, 9.32; N, 3.06.

**DiHDBP(6,6,8)**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.76 (bs, 2H), 8.67 (bs, 2H), 7.71 (d, J = 3 Hz, 4H), 7.60 (bs, 2H), 7.56 (bs, 2H), 4.37–4.25 (m, 24H), 2.10–1.95 (m, 24H), 1.77–1.31 (m, 96H), 0.94–0.88 (m, 30H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  152.93, 151.24, 151.15, 149.38, 149.35, 138.67, 138.57, 125.84, 125.70, 108.06, 107.91, 106.30, 69.60, 69.59, 69.21, 69.07, 68.83, 31.85, 31.56, 29.51, 29.48, 29.42, 29.38, 29.34, 28.92, 28.90, 26.20, 26.17, 25.75, 25.58, 22.69, 22.62, 14.10, 14.02. Mass (MALDI-TOF): *m*/ *z* 1901.381 [M + H<sup>+</sup>]. Anal. calcd for C<sub>122</sub>H<sub>186</sub>N<sub>4</sub>O<sub>12</sub>: C, 77.09; H, 9.86; N, 2.95. Found: C, 77.44; H, 10.04; N, 2.73.

**DiHDBP(6,6,10)**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.73 (s, 2H), 8.69 (s, 2H), 7.74 (s, 4H), 7.51 (s, 2H), 7.48 (s, 2H), 4.35–4.25 (m, 24H), 2.07–1.94 (m, 24H), 1.75–1.29 (m, 128H), 0.93–0.86 (m, 30H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 152.63, 152.61, 150.97, 150.94, 149.30, 139.45, 139.06, 139.02, 130.87, 128.79, 125.67, 125.63, 124.17, 107.99, 107.93, 106.76, 106.46, 69.66, 69.08, 69.04, 68.99, 68.72, 31.93, 31.55, 29.70, 29.63, 29.55, 29.53, 29.52, 29.44, 29.39, 28.97, 28.91, 26.20, 26.18, 25.75, 25.67, 22.69, 22.62, 14.11, 14.02. Mass (MALDI-TOF): m/z 2126.692 [M + H<sup>+</sup>]. Anal. calcd for C<sub>138</sub>H<sub>218</sub>N<sub>4</sub>O<sub>12</sub>: C, 77.99; H, 10.34; N, 2.64. Found: C, 77.50; H, 9.99; N, 2.30.

**DiHDBP(6,6,12)**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.77 (s, 2H), 8.65 (s, 2H), 7.71 (s, 4H), 7.56 (s, 2H), 7.50 (s, 2H), 4.35–4.25 (m, 24H), 2.07–1.94 (m, 24H), 1.75–1.28 (m, 160H), 0.94–0.87 (m, 30H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  152.55, 150.91, 150.87, 149.21, 139.35, 138.98, 138.93, 125.62, 125.57, 124.08, 124.06, 107.92, 107.86, 106.70, 106.31, 69.56, 69.03, 68.97, 68.92, 68.65, 31.92, 31.55, 29.74, 29.68, 29.56, 29.53, 29.44, 29.38, 28.93, 28.90, 26.19, 26.16, 25.73, 25.61, 22.68, 22.61, 14.09, 14.00. Mass (MALDI-TOF): *m/z* 2348.694 [M + H<sup>+</sup>]. Anal. calcd for C<sub>154</sub>H<sub>250</sub>N<sub>4</sub>O<sub>12</sub>: C, 78.72; H, 10.72; N, 2.38. Found: C, 78.37; H, 10.20; N, 2.01.

**DiHDBP(6,10,6)**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.75 (d, J = 2.0 Hz, 4H), 7.74 (s, 4H), 7.55 (bs, 4H), 4.34 (t, J = 6.5 Hz, 8H), 4.28–4.25 (m, 16H), 2.03–1.94 (m, 24H), 1.61–1.36 (m, 72H), 0.96–0.93 (m, 30H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  152.83, 151.04, 149.34, 139.23, 138.89, 125.70, 123.87, 107.97, 106.57, 106.38, 69.61, 69.14, 69.07, 31.68, 31.58, 29.51, 29.35, 29.29, 28.96, 28.89, 26.08, 25.84, 25.81, 25.75, 22.65, 22.62, 14.07, 14.04. Mass (MALDI-TOF): m/z 1732.615 [M + H<sup>+</sup>]. Anal. calcd for C<sub>110</sub>H<sub>162</sub>N<sub>4</sub>O<sub>12</sub>: C, 76.26; H, 9.42; N, 3.23. Found: C, 75.79; H, 9.44; N, 2.89.

**DiHDBP(6,12,6)**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.71 (d, J = 2.5 Hz, 4H), 7.72 (s, 4H), 7.50 (s, 4H), 4.33 (t, J = 6.5 Hz, 8H), 4.25 (t, J = 6.5 Hz, 16H), 2.00–1.93 (m, 24H), 1.63–1.36 (m, 76H), 0.96–0.91 (m, 30H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  152.65, 150.89, 149.23, 139.34, 139.00, 125.59, 124.08, 107.89, 106.69, 106.34, 69.56, 69.05, 68.98, 31.67, 31.66, 31.57, 29.61, 29.43, 29.35, 29.29, 28.96, 28.89, 26.08, 25.83, 25.79, 25.74, 22.63, 22.62, 22.61, 22.57, 14.04, 14.02. Mass (MALDI-TOF): *m/z* 1760.282 [M + H<sup>+</sup>]. (1759.2502 [M<sup>+</sup>] calculated for C<sub>112</sub>H<sub>166</sub>N<sub>4</sub>O<sub>12</sub>).

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