Tetrahedron 66 (2010) 8745–8755

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis and thermal properties of rigid oxa-bridged-containing dimers and tetramers

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ARTICLE INFO

Article history:
Received 21 April 2010
Received in revised form 1 September 2010
Accepted 1 September 2010
Available online 8 September 2010

ABSTRACT

Several symmetrical, linear dimers and some star-like tetramers were prepared using easily accessible oxa-bridged derivatives as central rigid cores. In order to produce new liquid crystalline materials various mesogenic/promesogenic groups, containing biphenyl-4,4′-diol, 4,4′-(diazene-1,2-diyl)diphenol and cholesterol sub-moieties, were connected through oxy-ethylene linkers via an ester linkage, in the end-on fashion. Their thermal behaviour and mesomorphic properties were investigated by differential scanning calorimetry (DSC), polarized optical microscope (POM), and variable temperature small-angle X-ray diffraction (XRD) methods. While essentially all the biphenyl-4,4′-diol- and 4,4′-(diazene-1,2-diyl)-based dimeric derivatives exhibited smectic liquid crystalline mesophases, the nature of which are mesogenic groups dependent, none of the cholesterol-containing compounds and tetramers were mesomorphic.

1. Introduction

Liquid-crystalline linear oligomers (dimers, trimers, etc.), as low molecular-weight model compounds of linear main-chain liquid crystal polymers, discovered during the 1980s, still remain the focus of recent research.[1] Liquid crystal dimers are molecules composed of two conventional mesogenic groups linked together via spacers of variable chemical natures. The dimers can be made symmetrical or unsymmetrical based on whether the two mesogenic end-units are identical or different.[1,2] Moreover, depending on the topology of attachment of the lateral mesogenic entities to the spacer (end-on or side-on types), dimers can approximate I-shape (two end-on mesogens), T-shape (an end-on and a side-on mesogens) or even H-shape (two side-on mesogens), leading to versatile molecular structures and a wide variety of supramolecular arrangements whose mesomorphic properties can be subtly modulated.[3] Several families of liquid-crystalline dimers have been prepared until now with a great choice of spacers, the most commonly used being a simple flexible alkyl chain (Fig. 1, **1**).[1,3,4] With the aim to modulate and control thermal and physico-chemical properties, mesogenic dimers incorporating siloxane fragments,[5] oxy-ethyelene and perfluorinated groups,[3] cyclic non rigid moieties, such as cyclohexane (Fig. 1, **2**),[6] pseudo-rigid molecular framework like bicyclo [2.2.2] octane (Fig. 1, **3**)[7] and cubane (Fig. 1, **4**),[8] or even carborane derivatives (Fig. 1, **5**)[9] have also been synthesized. Functional liquid crystal dimers successfully integrating active moieties, such as

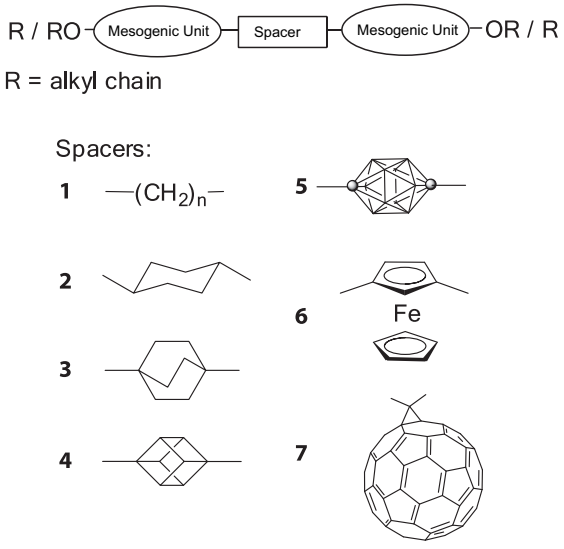

Fig. 1. Schematic representation of a selection of liquid-crystalline dimers with flexible and rigid spacers.

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doi:10.1016/j.tet.2010.09.003

imidazolium cation,[10] metallic fragments,[11] ferrocene (Fig. 1, **6**),[12] or fullerene (Fig. 1, **7**)[13] have also been reported. Incorporation of a rigid core as a spacer is believed to provide the necessary anisotropic interactions for the occurrence of the liquid crystalline phase and to a large extent, to dictate the properties of the bulk materials.[9b]

Recently, we have demonstrated an easy access to sterically constrained oxa-bridged derivatives.[14] We thought of utilizing oxa-bridged derivatives as the rigid central spacers to construct novel type of liquid-crystalline dimeric compounds and rationalize and analyze accordingly their thermal behaviours and optical properties. Our strategy consisted of incorporating the oxa-bridged derivatives **8**, **9** and **10** (Fig. 2) into liquid-crystalline dimers and tetramers by direct esterification methods with suitable mesogens.

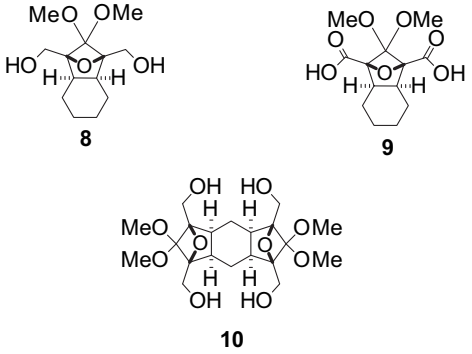
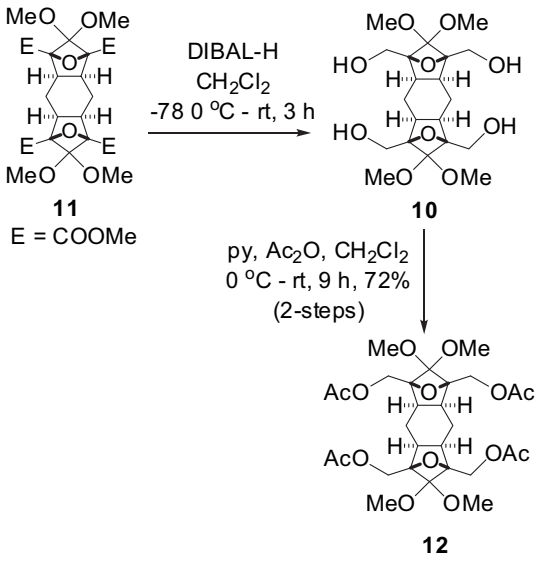


Fig. 2. Oxa-bridged core-derivatives.

2. Results and discussion

2.1. Synthesis of oxa-bridged compounds

The mono-oxa-bridged diol **8** was obtained by reducing dimethyl ester derivative of oxa-bridged compound **9**[14] with sodium borohydride in THF under reflux condition, a convenient method reported from our laboratory for related system.[15] A similar approach for the preparation of bis-oxa-bridged tetrol **10**, starting from the corresponding tetramethyl ester **11**,[14] furnished an isomeric mixture.[14] The tetrol **10** was finally obtained by treating **11** with DIBAL-H in dichloromethane (Scheme 1). For characterization purpose, the highly polar tetrol **10** was converted into its corresponding tetraacetate **12** in 72% overall yield.



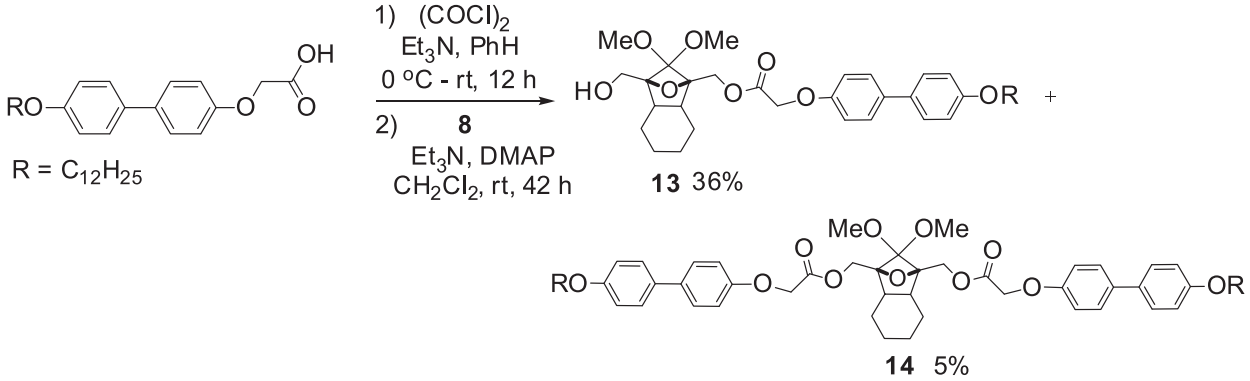
Scheme 1. Synthesis of tetrol **10** and its acetyl homologue **12.**

2.2. Synthesis of dimers

*2.2.1. Esterification of diol **8**.* Initial efforts to prepare ester derivatives of **8**–**10** with known mesogenic groups using conventional techniques (DCC/DMAP[4c,16] or via acid chloride[8,9b]) proved to be inefficient. When the coupling reaction between oxa-bridged diol **8** with 4-dodecyloxybenzoic acid was performed in presence of the DCC/DMAP (room temperature, 37 h), a mixture of mono-esterified product and the desired disubstituted product was obtained in 38% yield each. Surprisingly however, under the same reaction condition, coupling reaction between **8** and 2(4′-(dodecyloxy)biphenyl-4-yloxy)acetic acid afforded only the corresponding mono-esterified product in 30% yield. Finally, when the esterification reaction was performed between 2(4′-(dodecyloxy)biphenyl-4-yloxy)acetyl chloride and oxa-bridged diol **8** in presence of DMAP, only 5% of the desired product **14** and 36% of the mono-esterified product **13** were recovered (Scheme 2).

The mixed anhydride of the mesogenic acid, obtained by the treatment of 2(4′-(dodecyloxy)biphenyl-4-yloxy)acetic acid with 2-methylpropyl chlorocarbonate in triethylamine (room temperature, 5 h) in the presence of the diol **8**, at room temperature first for 6 h, and then at reflux temperature (THF) for 10 h, did not react to yield the corresponding dimer **14**.

*2.2.2. Esterification of oxa-bridged diacid **9** using 2,4,6-trichlorobenzoyl chloride.* The poor efficiency of the esterification of **8** led us to consider the oxa-bridged diacid **9** instead. Following a literature precedent from cubane chemistry,[8] we first attempted esterification via the acid chloride route. The acid chloride of **9**, prepared in situ from $(COCl)_2$ in Et_3N/CH_2Cl_2 at 0 °C and then at room temperature for 5 h, reacted at reflux in pyridine/CH_2Cl_2 for



Scheme 2. Synthesis of dimer **14**.

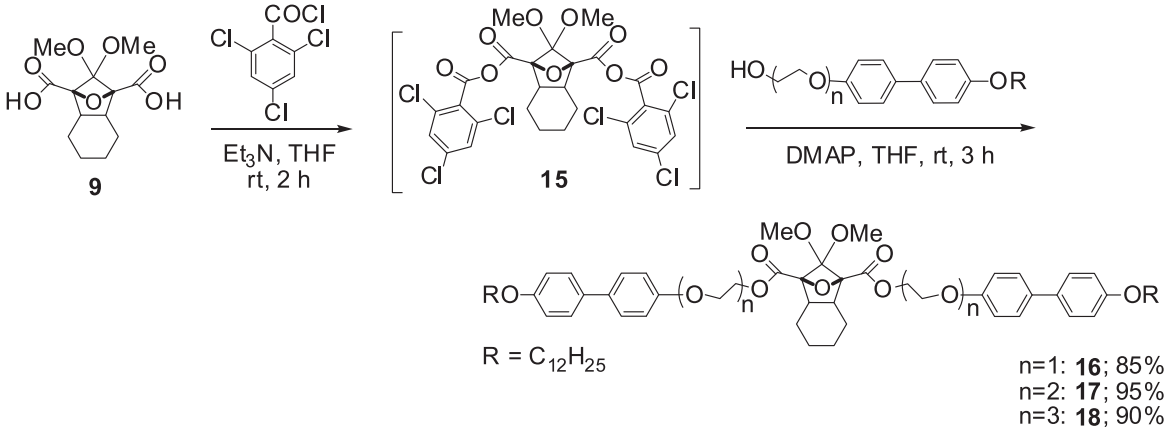
2 h with 1-octanol to give the corresponding diester in moderate yield (45%), whilst the same reaction with 4′-(dodecyloxy)biphenyl-4-ol failed.

The dimers with rigid oxa-bridged spacer were finally obtained by treating the mixed anhydride formed from diacid **9** and 2,4,6-trichlorobenzoyl chloride (Yamaguchi reagent,[17] widely used for the macrocyclisation in multistep synthesis) with the appropriate alcohol counterpart. As depicted in Scheme 3, the oxa-bridged diacid **9** was first treated with the 2,4,6-trichlorobenzoyl chloride in presence of triethylamine in THF for 2 h at room temperature and the resulting crude mixed anhydride **15** was exposed to 2-(4′-dodecyloxy-biphenyl-4-yloxy)-ethanol in presence of DMAP to obtain the desired product **16** in excellent yield. Increasing the number of oxy-ethylene units ($-CH_2CH_2-O-$) did not affect the yield of the products (**17** and **18**, Scheme 3). Similarly, reaction of mixed anhydride **15** with various 2[4-(4-dodecyloxy-phenylazo)-phenoxy]-ethanol oxyethylene homologues afforded the desired materials, **19**, **20** and **21**, in good yields (Scheme 4).

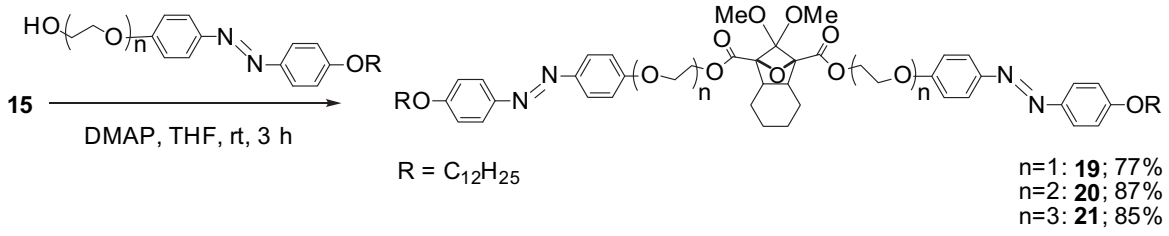
Liquid crystals derived from naturally occurring cholesterol represent an exemplary and emerging class of chiral liquid crystals, which may find practical and useful utility in various applications.[18] From literature, cholesterol moiety containing molecules generally show chiral nematic (or cholesteric) mesophase.[3,19] We synthesized cholesterol-based symmetric dimers with the rigid oxa-bridged spacer **9**. As illustrated in Scheme 5, mixed anhydride **15** treated with cholesterol, or derivatives having two or three oxy-ethylene units, afforded good to excellent yields (**22**, **23** and **24**).

2.3. Synthesis of tetramers

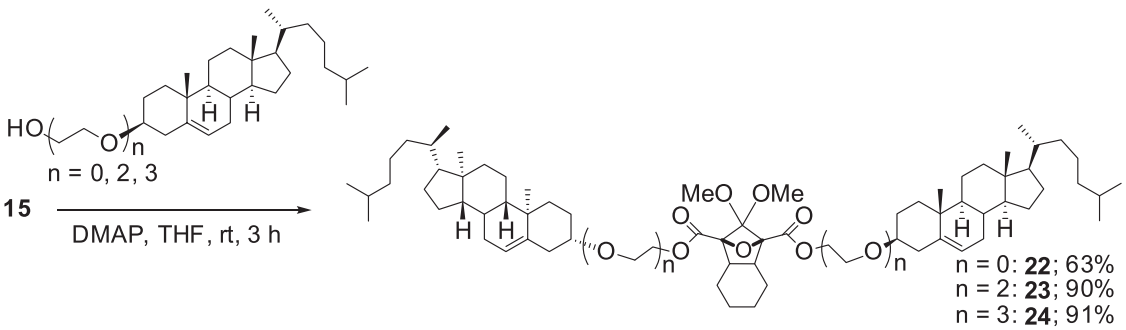
Using the same procedure, three tetramers derived from bis-oxa-bridged tetrol **10** were successfully prepared. The mixed anhydrides of 2-(4′-(dodecyloxy)biphenyl-4-yloxy)acetic acid, 10-(biphenyl-4-yloxy)decanoic acid and cholesterol-derived acid with 2,4,6-trichlorobenzoyl chloride were treated with bis-oxa-bridged tetrol **10** in presence of DMAP to afford the tetramers **25**, **26** and **27** (Fig. 3), respectively, in good yields.



Scheme 3. Synthesis of dimers **16**–**18** biphenylene-based mesogens.



Scheme 4. Synthesis of dimers **19**–**21** azobenzene-based mesogens.



Scheme 5. Synthesis of dimers **22**–**24** cholesterol-based mesogens.

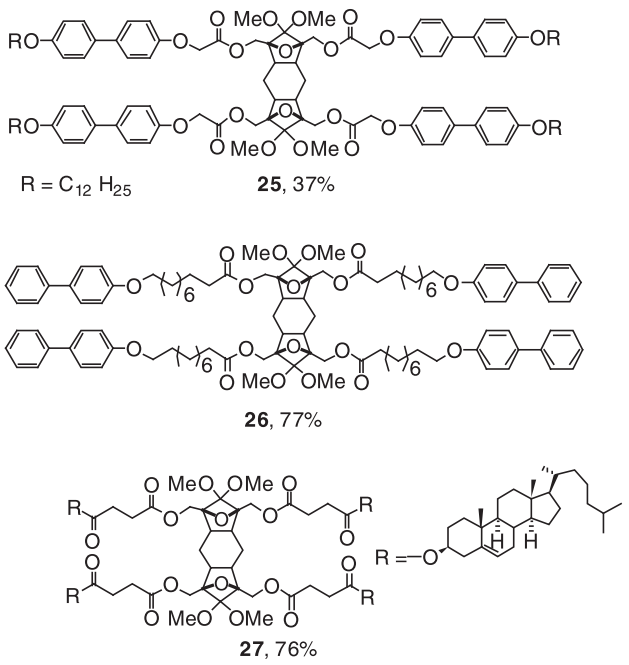


Fig. 3. Tetramers synthesized from oxa-bridged spacer **10**.

3. Mesomorphic behaviour

Having successfully synthesized various symmetrical oligomers bearing liquid crystalline side-groups, their physico-chemical properties were investigated. The thermal behaviour was analyzed by differential scanning calorimetry (DSC) with heating/cooling rate of 5 °C/min, optical textures were observed using polarized optical microscope (POM) at variable temperatures and the structures of the mesophases analyzed by temperature-dependent small-angle X-ray diffraction analysis. The transition temperatures and the phase behaviour of the nine symmetrical dimers and three tetramers are collected in Table 1.

In the case of the dimers three different mesogenic units were linked via an oxy-ethylene spacer with increasing number of segments. Clearly, it became quickly apparent that the mesophase behaviour of the dimers was strongly dependent on the mesogenic group nature as well as on the length of the connecting group.

3.1. Dimers-based 4′-(dodecyloxy)biphenyl-4-ol (16, 17, 18)

The three dimeric systems having the oxa-bridged core linked on both side with 4′-(dodecyloxy)biphenyl-4-ol were investigated as a function of the spacer length. Compound **16**, with one oxyethylene segment, was obtained as a colourless floppy solid at room temperature. DSC analysis revealed (Fig. 4a) a complex thermal behaviour. On heating, an endothermic peak centred at 57 °C, followed by small events (corresponding to successive crystallizations and meltings between approximately 75–80 °C and 70–100 °C,

Table 1
Thermal properties of oxa-bridged dimers **16**–**21** and tetramers **25**–**27**[a]

Entry	Compound	Heating	Cooling
1	**16**	Cr 57 (50.6) *M* ~70 (−)[b] Cr′ ~80 (−)[b] Cr″ ~85 (−)[b] Cr‴ 100 (31.3) I	I 74 (−10.7) Cr′ 37 (−3.9) Cr
2	**17**	Cr 66 (26.1) SmA 84 (10.1) I	I 82 −9.5) SmA 59 (−24.3) Cr
3	**18**	Cr 64 (24.5)[c] SmA 75 (8.4) I	I 74 (−8.6) SmA 62 (−26.6) Cr
4	**19**	Cr 109 (38.9) SmC 129 (1.9) I	I 119 (−)[d] SmC 78 (−4.1) Cr′ 58 (−1.3) Cr
5	**20**	Cr 71 (−)[c] Cr′ 76 (29.6)[e] SmC 95 (3.6) I	I 90 (−)[d] SmC 74 (−5.5) Cr′ 56 (−15.5) Cr
6	**21**	Cr 60 (5.4) SmF/I 72 (−)[c] SmC 73 (20.9)[e] I	I 70 (−)[d] SmC 64 (−)[c] SmF/I 60(−22.1)[e] Cr
7	**22**	Cr 258 (76.3) I	I 189 (−39.4) Cr
8	**23**	Cr 169 (36.3) I	I 143 (−18.2) Cr
9	**24**	I	I
10	**25**	Cr 177 (18.6) I	I 125 (−24.5) Cr
11[b]	**26**	Cr 90 (22.3) I	I
12	**27**	Cr 192 (21.9) I	I 141 (−7.1) Cr

[a] Phase transition peak temperatures (°C) and associated enthalpy changes (kJ mol^{-1} in parentheses). Cr, Cr′, Cr″, Cr‴=crystalline phases, SmA/C/F/I=smectic A/C/F/I phases, M=unidentified phase, I=isotropic.
[b] Not measured.
[c] Unresolved peaks.
[d] Transition was observed under microscope but too weak to be detected by DSC on cooling.
[e] Cumulated enthalpies: Cr–Cr′ for **20** and SmF–SmC for **21**.

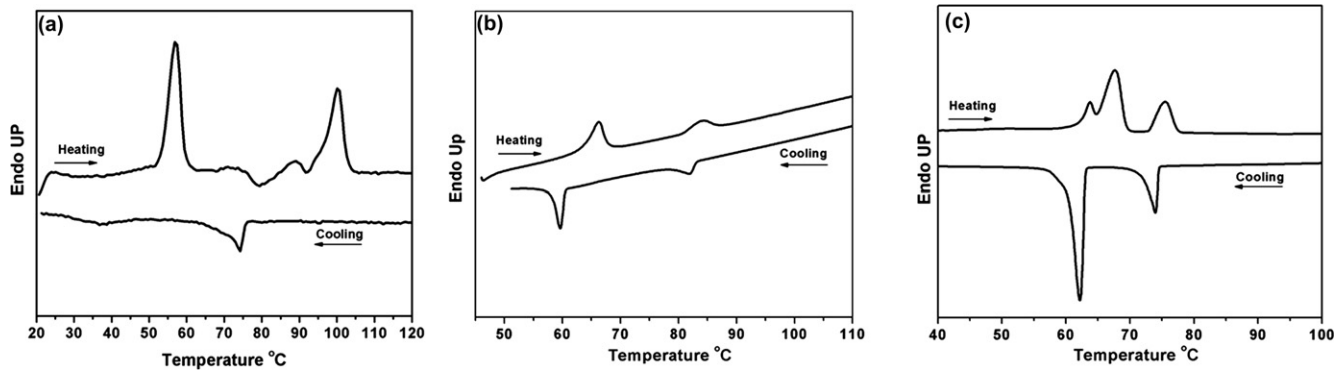


Fig. 4. DSC traces of (a) compound **16** (b) compound **17** and (c) compound **18**.

respectively) and a broad peak at 100 °C were observed. On cooling from the isotropic liquid phase, only two exothermic peaks were seen at 74 °C and at 37 °C, respectively. POM carried out during heating, despite the observation of remnant birefringence when light pressure was applied onto the glass cover slip, was not sufficiently relevant to properly identify this complex phase behaviour (Fig. 5a). The high value for the melting enthalpy transition at ca. 100 °C (Table 1), suggesting a transition between a high-ordered structure into the isotropic liquid, and the important supercooling effects were however strong indications of the absence of mesomorphism.

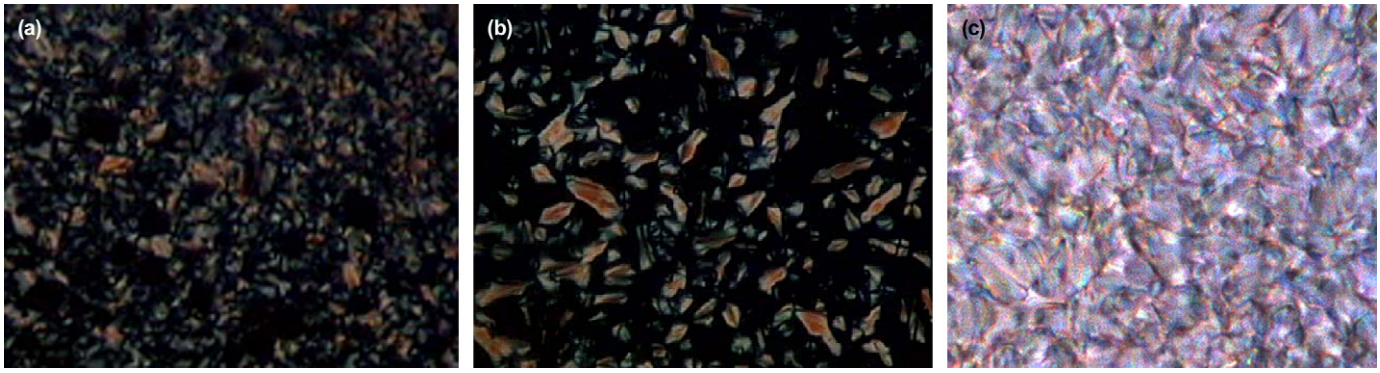


Fig. 5. POM texture of (a) compound **16** at 68 °C (b) compound **17** at 79 °C and (c) compound **18** at 72 °C.

Compounds **17** and **18** (with two and three oxy-ethylene fragments spacers, respectively, between the oxabridge and the mesogenic units) were also obtained as colourless solids. DSC traces (Fig. 4b and c) showed exothermic transitions with melting peaks temperatures at 66 and at 64 °C and clearing peaks temperatures at 84 °C and 75 °C for **17** and **18**, respectively. These transitions were fully reversible on cooling, with little supercooling effects. POM textures observed on cooling were consistent with the presence of a fluid mesophase (Fig. 5b and c), and the observation of needle-like defects and large homeotropic zones were reminiscent of orthogonal smectic phase (e.g., SmA or SmB type). Continuing cooling further, the mesophases reversibly transformed into crystalline solids.

The complex thermal behaviour of **16** was analyzed by X-ray diffraction at various temperatures and was found to be consistent with DSC measurements. Between room temperature and up to a temperature <60 °C, a poorly crystallized state was deduced (likely corresponding to locally entangled amorphous and semi-organized domains), as evidenced by the detection of broad diffusions in the small-angle part and sharp reflections in the wide- and mid-angle parts (a few intense, not-too-sharp diffraction peaks at 11.0, 4.7, 4.3 and 3.7 Å were measured, Fig. 6, T=50 °C). When heating was continued above 60 °C, the X-ray pattern was modified, indicating the transformation of the structure into a more organized intermediate phase. The diffractogram recorded at T=60 °C (Fig. 6) exhibited two sharp and intense small-angle peaks, with the reciprocal spacings in the ratio 1:2 (d_{001}=62.2 and d_{002}=31.0 Å), characterizing a lamellar morphology with an average interlayer periodicity d=62.1 Å, of the same magnitude of the length of the molecule in its stretched conformation (ca. 60–65 Å). In addition, two broad wide-angle diffusions (8.0–9.0 and 4.6 Å) were also detected, corresponding, respectively, to weak molecular fluctuations and lateral short-range ordering of the molten chains and biphenylene units. The deconvolution of the peak in the wide-angle at 4.6 Å revealed that it consisted in fact of the superimposition of two signals, namely a broad one that characterizing the molten chains, and a weaker but sharper peak (h_0=4.6 Å, see peak deconvolution in Fig. 6), reflecting a supplementary short-range ordering of the mesogenic arms within the sub-layers, likely with a hexagonal symmetry (vide infra). Considering a density close to 1 for partially molten **16**, the molecular area (obtained from the ratio of the molecular volume[20] by the smectic periodicity, $A=V/d$=1740 Å^3/62.1 Å=28 Å^2) is fairly compatible with the transverse area of one biphenylene unit calculated in an orthogonal-like lamellar phase with a hexagonal in-layer ordering (hexagonal cross-section area: $4.6\times4.6\times2/\sqrt{3}$=24.4 Å^2), and suggests that the dimer adopts a fully stretched conformation with the mesogen units on each side of the oxabridge, parallel to the layer normal. At ca. 70 °C, the sample melts and immediately recrystallizes (T=75 °C) before melting again at ca. 85–90 °C into another metastable phase, immediately transforming into the isotropic liquid at ca. 100 °C (Fig. 6). On cooling from the isotropic liquid, no sign of such a behaviour was detected, nor was a mesophase evidenced by XRD, and only crystalline phases formed below 74 °C. This complicated thermal behaviour is reversible on subsequent heat-cool cycles (after annealing at room temperature for several hours), and therefore the mesophase detected for **16** can be qualified as re-entrant or transient. Such behaviour is quite rare, although it has been observed sometimes with few compounds possessing complicated molecular structures or for compounds whose molecular structures change reversibly with temperature.

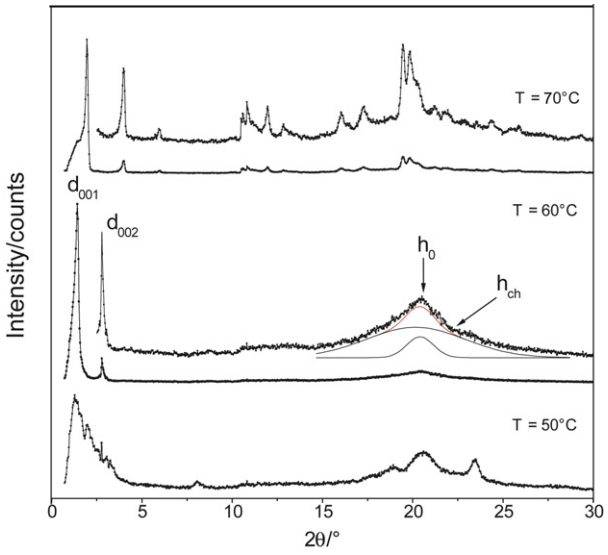


Fig. 6. Diffractograms of compound **16** recorded at various temperatures (T=50, 60, 70 °C); deconvolution of the wide-angle peak into the diffuse Gaussian scattering halo (short-range order of the chains in their melted conformation) and sharp peak corresponding to some local in-layer ordering.

A possible explanation may be rather the high viscosity of the system combined with the enhancement of the segregation at the molecular scale: the dimers likely first self-organize into a smectic mesophase, and then due to this specific lamellar organization, crystallization is favoured. As shown in the diffractogram at T=70 °C (Fig. 6), a lamellar crystal phase can be detected with sharp peaks at 44.4, 22.1, 14.8 Å in the ratio 1:2:3 (and several sharp peak in the wide-angle part, corresponding to chains and mesogens crystallization). The reduction of the layer periodicity in this case is attributed to interdigitation and/or tilt of the mesogenic groups.

The smectic behaviour was confirmed for both compounds **17** and **18** by XRD (Figs. 7 and 8): two sharp small-angle peaks, with the reciprocal spacings in the ratio 1:2 (d_{001}=57.7 and d_{002}=28.94 Å for **17** and d_{001}=65.57 and d_{002}=32.57 Å for **18**), characterizing a lamellar morphology with interlayer periodicities d=57.8 and 65.35 Å, respectively, and two broad wide-angle diffusions (8.0–9.0 and 4.6 Å), corresponding, respectively, to weak molecular fluctuations (oxa-bridged core) and lateral short-range ordering of the molten chains and biphenylene units. Again, the molecules are likely in a fully stretched conformation and lie quasi parallel to the smectic layer normal, as supported by the molecular areas values (A=32.6 and 31.1 Å^2, respectively), in agreement with a disordered smectic phase with orthogonal symmetry (i.e., SmA).

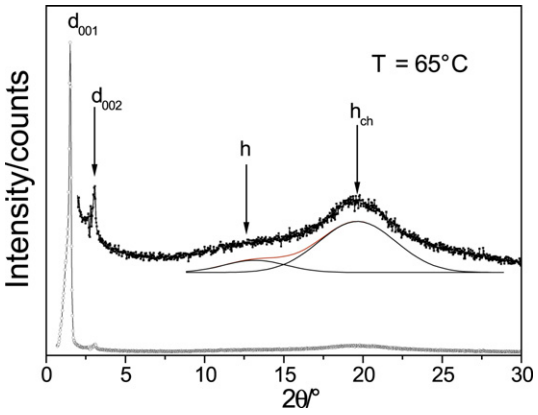


Fig. 7. X-ray diffraction patterns of compound **17** (at T=65 °C on cooling, SmA phase); the diffuse scattering halos are fitted by a Gaussian function in agreement with the short-range order of the chains in their melted conformation.

Thus, to conclude, the lengthening of the pegylated segment from one to two units contributes to a substantial enhancement of the mesophase stability in this series of oxa-bridged dimers. Whilst **16** shows a complicated thermal behaviour, **17** in contrast exhibits an enantiotropic mesophase between 66 and 84 °C. Whereas **18** is still mesomorphic, its mesophase stability temperature range has been substantially reduced by almost 10 °C, when compared to **17**. These results emphasize the strong mesomorphism sensitivity to the extended coupling between both the central core and mesogens. The mesophases are formed by the lateral two-dimensional registry of the dimeric molecules in cylindrical conformation, with the mesogenic groups oriented quasi parallelly to the layer normal. Alternatively, they may also adopt the shape of a hairpin, and in this case would form a head-to-head pair to generate the cylindrical shape; note that X-ray experiment does not allow distinction between both conformations.

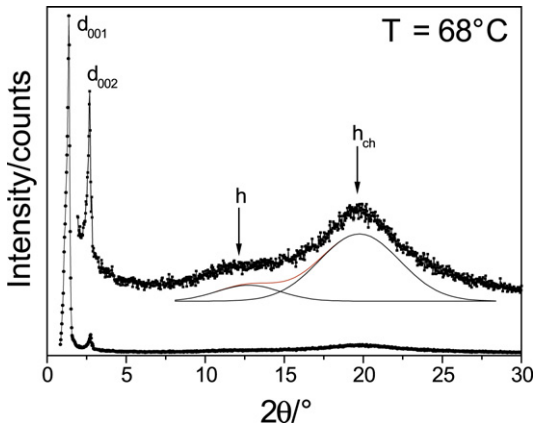


Fig. 8. Diffractogram of compound **18** (at T=68 °C on cooling, SmA phase); the diffuse scattering halos are fitted by a Gaussian function in agreement with the short-range order of the chains in their melted conformation.

3.2. Dimers-based 4{[4-(dodecyloxy)phenyl]diazenyl}phenol (19, 20, 21)

All the compounds of this series, **19**–**21**, having the oxa-bridged core linked at both sides with 4{[4-(dodecyloxy)phenyl]diazenyl} phenol with one (**19**), two (**20**) or three (**21**) oxy-ethylene chain spacers, were obtained as a yellowish floppy solid at room temperature. For compound **19**, the DSC analysis revealed (Fig. 9a) two endothermic peaks at 109 °C and at 129 °C. On cooling from the isotropic phase, two exothermic transitions were observed at 78 °C (for the crystallization) and at 58 °C (for a transition from one crystal to another crystal phase); the isotropic-mesophase transition was not detected by this technique. Again POM analysis alone was not relevant for phase identification, although, a birefringent fluid mesophase was observed. DSC traces of **20** showed three endothermic transitions at 71, 76 (although both peaks are fused and not resolvable) and at 95 °C (Fig. 9b). On cooling from the

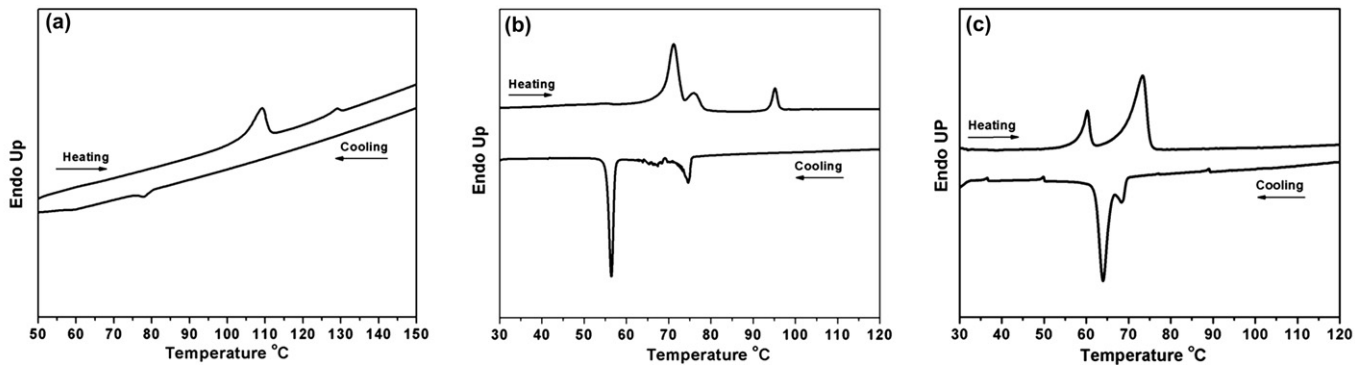


Fig. 9. DSC traces of (a) compound **19**, (b) compound **20** and (c) compound **21**.

isotropic phase, exothermic peaks at 74 °C and at 56 °C were observed; again isotropization at 90 °C was not detected. By POM analysis, a texture reminiscent to that of the SmC-type phase was recognized (at around 79 °C on heating): locally some schlieren-like as well as broken focal-conic fan textures were observed simultaneously on cooling from the isotropic phase between clean glass substrates.[21] Finally, DSC analysis of **21** (Fig. 9c) showed two transitions, a sharp endothermic peak centred at 60 °C and a broad peak at ca. 73 °C. On cooling, two major exothermic peaks could be recorded, at ca. 70 °C and around 64 °C. A birefringent and fluid texture was observed by POM, although totally irrelevant for mesophase assignment.

XRD experiments confirmed in all cases the presence of smectic phases, expected on the basis of the molecular shape of the terms of this series. Diffractogram of compound **19** (Fig. 10a) recorded on cooling at 104 °C, exhibits a single sharp reflection in the small-angle ($d=d_{001}$=30.9 Å), corresponding to the smectic periodicity, were detected by XRD for compound **21**. The high-temperature phase (recorded on cooling at 68 °C, Fig. 10d) corresponds to a disordered tilted smectic phase, SmC (d_{001}=54.7 and d_{002}=27.26, h_{ch}=4.55 Å, A=38.9 Å^2). Whereas the low-temperature phase, whilst still smectic (d_{001}=55.2 and d_{002}=27.8, d_{003}=18.3, h_0=4.2, h_{ch}=4.55 Å, A=38.9 Å^2), possesses additional local in-layer ordering: the presence of the intense reflection h_0 suggests hexatic type of organization within the layer, and since the molecules are still tilted within the layer, the mesophase can be assigned to as SmF or SmI phase (tilted hexatic phase), not yet distinguishable.[19,22]

From the above experiments, the three samples exhibit liquid crystalline smectic phases, all assigned as SmC phase, with an additional SmI/F phase in one case. On increasing the oxy-ethylene chain length from 1 to 3 segments (**19**→**21**), the transition temperatures were considerably affected, with a net decrease of both the melting and the clearing temperatures from 109 to 60 °C and from 129 °C to 73 °C, respectively, and thus leading concomitantly

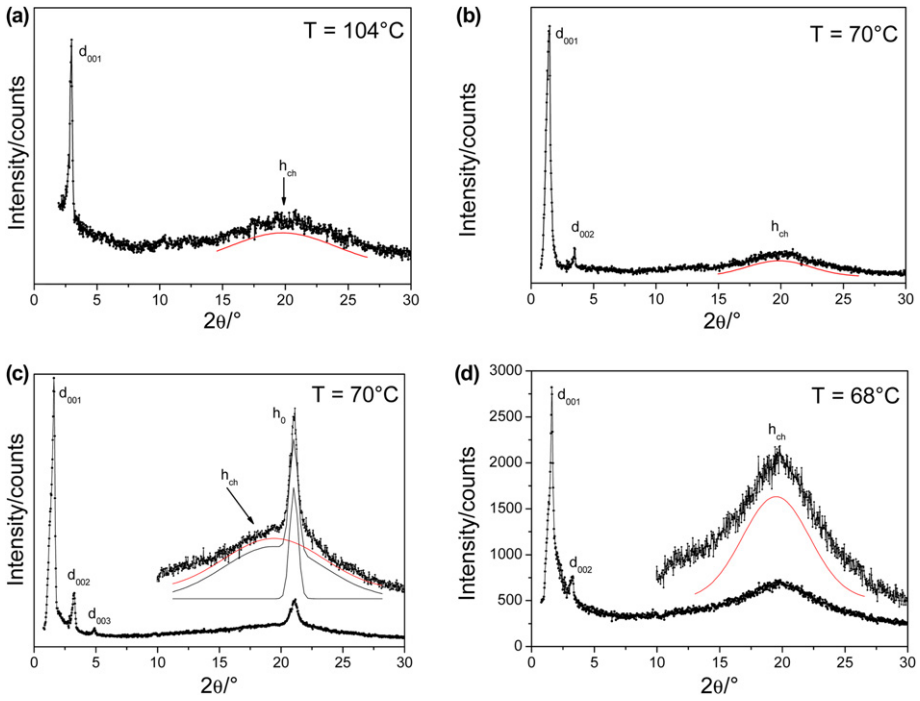


Fig. 10. X-ray diffraction patterns of (a) compound **19** (at T=104 °C on cooling, SmC phase), (b) compound **20** (at T=70 °C on cooling, SmC phase), and (c) compound **21** (at T=70 °C on heating, SmF/I phase) and (d) compound **21** (at T=68 °C on cooling, SmC phase); Gaussian fits for the molten chains signals, and peak deconvolution.

and the broad scattering at ca. 4.6 Å corresponding to the molten aliphatic chains. The periodicity being much smaller than the molecular length (ca. 60–65 Å), the mesogenic arms ought to be highly tilted with respect to the layer normal. Indeed, a rough estimation of the molecular volume considering a density of 1 g cm^3, gives a large value of the cross-section area of 59 Å^2, implying a substantial tilt of the rigid cores in order to be able to compensate the rather large expansion of the transverse chain area, in agreement with a SmC-type mesophase. Either, the entire molecule, in its fully stretched conformation, is tilted within the layer, or the dimer adopts a bow-shape.[1] As for compound **20**, two sharp small-angle reflections in the ratio 1:2 (d_{001}=46.58 and d_{002}=23.27 Å) of a lamellar structure along the broad diffusion at ca. 4.6 Å were detected in the diffractogram (Fig. 10b), confirming again the smectic nature of the mesophase: the periodicity, 46.6 Å, smaller than the molecular length, conveys to a SmC phase. As above, the cross-section area is large, with a value of 42.5 Å^2, which suggests important tilt of the anisotropic end-groups within the layers. Finally, two mesophases to a substantial diminution of the mesophase temperature range. In all cases, a substantial tilt of the rigid cores, necessary to compensate the rather large expansion of the transverse chain area, has been deduced from XRD experiments. Such compensation may be achieved in two ways: either, the entire molecule, in its fully stretched conformation (or head-to-head pairs), is tilted within the layer, or it adopts the shape of a bow. As above, the mesophases are formed by the lateral two-dimensional registry of the dimers but with the mesogenic groups tilted with the layer normal.

3.3. Dimers-based on cholesterol (22, 23, 24)

The oxa-bridged compounds derived from cholesterol only showed one transition peak by DSC, at 258 °C for **22**, and 169 °C for **23**; **24** was obtained at a room temperature oil. The unexpected absence of mesomorphic behaviour was confirmed by POM analysis. Moreover, on increasing the spacer length, the crystalline phase stability is drastically reduced. A possible explanation for the

lack of liquid-crystalline behaviour may be connected to the bulkiness of the cholesterol substituents, which hinders the ideal packing of the molecules into layers.

3.4. Tetramers (25, 26, 27)

DSC analysis of the three tetramers (**25**–**27**) showed a single broad peak at 177 °C (**25**), 90 °C (**26**) and 192 °C (**27**), with strong supercooling for **25** (125 °C) and **27** (141 °C). The absence of mesophase was corroborated by POM, for which no specific texture, although reminiscent of crystalline or highly ordered arrangements (sharp defects), below the clearing temperatures were revealed. Here the low flexibility of the core, the mismatch between transverse cross-sections of the various molecular parts and inappropriate spacer lengths between the mesogenic side-arms and central multivalent cores may be responsible for the loss of liquid crystalline properties.

4. Conclusion

In conclusion, several dimers and tetramers built up around original and rigid oxa-bridged cores have been prepared for the first time. We demonstrated that such a bulky central unit was not detrimental to the formation of liquid-crystalline mesophases. Indeed, induction of various low-temperature smectic phases (SmA/C/F/I) was confirmed for most dimeric compounds and their structure and stability were found to depend strongly on the end-mesogen type and spacer length. By XRD, it was shown that dimers with 4′-(dodecyloxy)biphenyl-4-ol as mesogenic end-unit exhibit an orthogonal smectic (SmA) liquid-crystalline phase, whilst the 4-((4-(alkyloxy)phenyl)diazenyl)phenol-containing dimers show a SmC mesophase (and for the longer chain homologue, an additional low-temperature SmF/I). In contrast, dimers derived from the cholesterol moieties as well as the tetramers have failed to exhibit liquid crystalline property. Within each mesomorphic series, the maximum stability temperature range of mesophases was obtained for mid-spacer chain-lengths, and azo-containing compounds are more prone to phase induction than biphenyl-based derivatives.

5. Experimental

5.1. General

All the reactions were performed in oven dried apparatus and the reaction mixtures were magnetically stirred. Reactions were monitored using thin layer chromatography (TLC), performed on silica gel coated on microscopic slides and visualized under UV light or exposure to iodine. Column chromatography was performed using silica gel (100–200 mesh) and ethyl acetate/hexane was used as an eluent unless otherwise mentioned. Evaporation of solvent was performed at reduced pressure, using a rotary evaporator. Melting points recorded are uncorrected. IR spectra were recorded as KBr pellets (solids) or thin films (liquids). ^{1}H NMR and proton-decoupled ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, on JEOL spectrophotometer. Data are reported as follows: (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet; coupling constant(s) in hertz). Samples for NMR were made in $CDCl_3$; tetramethylsilane was used as the internal standard. Mass spectra were recorded on WATERS-HAB213 mass spectrometer. Commercial grade solvents were distilled before use. Ethyl acetate was distilled over anhydrous sodium carbonate. Dichloromethane was distilled over phosphorous pentoxide and stored over 4 Å molecular sieves. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen. Benzene was refluxed and dried over sodium. Triethylamine, pyridine was distilled and stored over potassium hydroxide pellets. Methanol and ethanol were refluxed and distilled over magnesium turnings and stored over 4 Å molecular sieves. Distilled water was used for aqueous work-up. Differential scanning calorimeter (DSC) was recorded in Perkin–Elmer DSC 6. The identification of the mesophases and the transition temperatures of the compounds were determined using a polarizing microscope (Leica DM2500P) in conjunction with a programmable hot stage (Linkam THMS600). The XRD patterns were obtained with two different experimental set-ups. In all cases, a linear, monochromatic Cu Kα1 beam (λ=1.5405 Å) was obtained using a sealed-tube generator (900 W) equipped with a bent quartz monochromator. In the first set, the transmission Guinier geometry was used, whereas a Debye–Scherrer-like geometry was used in the second experimental set-up. The crude powder was filled in Lindemann capillaries of 1 mm diameter and 10 μm wall thickness.

*5.1.1. Compounds **13**–**14**.* To a stirred suspension of 2-(4′-(dodecyl) biphenyl-4-yloxy)acetic acid (41 mg, 0.099 mmol) in benzene (2 mL) were added oxalyl chloride (0.5 mL) and a drop of DMF. The reaction mixture was stirred at room temperature for 12 h. The volatiles were removed under vacuum and crude acid chloride was dissolved in dry dichloromethane (3 mL) and added to the mixture of diol **8** (10 mg, 0.038 mmol), triethylamine (0.15 mL) and DMAP (0.5 mg) in dichloromethane (2 mL). The reaction mixture was stirred for 42 h at room temperature under argon atmosphere and then quenched by adding distilled water (5 mL). The solution was extracted with dichloromethane (2×4 mL) and the combined organic layers were washed with distilled water (1×2 mL), brine solution (2 mL) and then dried over anhydrous sodium sulfate, filtered and concentrated afforded the crude product, which on purification by silica gel column chromatography using 10–40% ethyl acetate/hexane afforded compound **13** (9 mg, 36%) and compound **14** (2 mg, 5%). Compound **13**: viscous solid; R_f (25% ethyl acetate/hexane) 0.30; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.36 (m, 4H), 6.88–6.85 (m, 4H), 4.63 (s, 2H), 4.35 (dd, J=12.2, 17.0 Hz, 2H), 3.91 (t, J=6.6 Hz, 2H), 3.79 (dd, J=12.9, 27 Hz, 2H), 3.45 (s, 3H), 3.18 (s, 3H), 2.22–2.21 (m, 2H), 1.76–1.63 (m, 8H), 1.39–1.19 (m, 20H), 0.81 (t, J=6.6 Hz, 3H). Compound **14**: colourless solid; mp: 78 °C; R_f (25% ethyl acetate/hexane) 0.60; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47–7.43 (m, 8H), 6.95–6.91 (m, 8H), 4.69 (s, 4H), 4.41–4.4 (m, 4H), 3.98 (t, J=6.6 Hz, 4H), 3.35 (s, 3H), 3.17 (s, 3H), 2.26 (m, 2H), 1.83–1.76 (m, 4H), 1.46–1.44 (m, 4H), 1.27 (m, 40H), 0.88 (t, J=6.6 Hz, 6H).

5.2. General procedure for the preparation of compounds 16–18

To a mixture of oxa-bridged diacid **9** (200 mg, 0.7 mmol), triethylamine (177 mg, 1.75 mmol) in THF (4 mL) was added 2,4,6-trichlorobenzoyl chloride (350 mg, 1.43 mmol). The reaction mixture was stirred at room temperature for 2 h and resultant solution was then added to a mixture of 2-(4′-(dodecyloxy)biphenyl-4-yloxy)ethanol (641 mg, 1.61 mmol) and DMAP (197 mg, 1.61 mmol) in THF (6 mL). The reaction mixture was stirred at room temperature for 3 h under argon atmosphere. After reaction was completed, sodium bicarbonate solution (3 mL) was added followed by distilled water (15 mL). The solution was extracted with ethyl acetate (4×4 mL) and the combined organic layers were washed with distilled water (3×3 mL), brine solution (3 mL) and dried over anhydrous sodium sulfate, filtered and concentrated afforded the crude product, which on purification on silica gel column chromatography using 20% ethyl acetate/hexane afforded **16** (621 mg, 85%).

*5.2.1. Compound **16**.* Colourless solid; mp: 92 °C; R_f (30% ethyl acetate/hexane) 0.40; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.35 (m, 8H),

6.87–6.81 (m, 8H), 4.61–4.57 (m, 2H), 4.44–4.40 (m, 2H), 4.16–4.14 (m, 4H), 3.91–3.88 (m, 4H), 3.37 (s, 3H), 3.25 (s, 3H), 2.64–2.63 (m, 2H), 1.73–1.56 (m, 6H), 138–1.19 (m, 42H), 0.86–0.78 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2 (2C), 158.3 (2C), 157.3 (2C), 133.99 (2C), 132.97 (2C), 127.7 (4C), 127.6 (4C), 114.72 (4C), 114.69 (4C), 110.2, 92 (2C), 68 (2C), 65.5 (2C), 63.3 (2C), 52.1, 51.6, 41.9 (2C), 31.9 (2C), 29.62 (2C), 29.6 (2C), 29.57 (4C), 29.4 (2C), 29.3 (2C), 29.2 (2C), 26 (2C), 22.6 (2C), 17.8 (2C), 17.5 (2C), 14.1 (2C); IR (KBr): 2850, 1720, 1600, 1500, 1460, 1220 cm^{-1}; HRMS (ESI): m/z (M+H)$^+$ calculated for $C_{65}H_{90}O_{11}$: 1047.6561; found: 1047.6564.

5.2.2. Compound ***17***. Yield: 95%; colourless solid; mp: 54 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J=8.6 Hz, 8H), 6.86 (d, J=8.6 Hz, 8H), 4.4–4.38 (m, 2H), 4.28–4.2 (m, 2H), 4.0 (t, J=4.4 Hz, 4H), 3.9 (t, J=6.6 Hz, 4H), 3.77–3.71 (m, 8H), 3.37 (s, 3H), 3.26 (s, 3H), 2.64–2.61 (m, 2H), 1.75–1.54 (m, 6H), 1.4–1.19 (m, 42H), 0.82–0.79 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3 (2C), 158.3 (2C), 157.7 (2C), 133.8 (2C), 133.1 (2C), 127.6 (8C), 114.8 (4C), 114.7 (4C), 110.2, 92 (2C), 69.6 (2C), 68.9 (2C), 68.1 (2C), 67.5 (2C), 63.9 (2C), 52.1, 51.6, 41.9 (2C), 31.9 (2C), 29.5 (8C), 29.3 (6C), 26 (2C), 22.6 (2C), 17.9 (2C), 17.6 (2C), 14.1 (2C); IR (KBr): 2850, 1720, 1600, 1490, 1220 cm^{-1}; HRMS (ESI): m/z (M+H)$^+$ calculated for $C_{69}H_{98}O_{13}$: 1135.7085; found: 1135.7085.

5.2.3. Compound ***18***. Yield: 90%; colourless solid, mp: 61 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ; 7.37 (d, J=8.5 Hz, 8H), 6.89–6.85 (m, 8H), 4.38–4.33 (m, 2H), 4.25–4.19 (m, 2H), 4.07 (t, J=5.8 Hz, 4H), 3.89 (t, J=6.6 Hz, 4H), 3.77 (t, J=4.8 Hz, 4H), 3.64–3.57 (m, 12H), 3.37 (s, 3H), 3.26 (s, 3H), 2.64–2.61 (m, 2H), 1.73–1.69 (m, 8H), 1.29–1.19 (m, 40H), 0.8 (t, J=6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3 (2C), 158.3 (2C), 157.9 (2C), 133.7 (2C), 133.2 (2C), 127.6 (8C), 114.9 (4C), 114.8 (4C), 110.2, 92 (2C), 70.8 (2C), 70.6 (2C), 69.8 (2C), 68.8 (2C), 68.1 (2C), 67.6 (2C), 63.9 (2C), 52.1, 51.6, 41.9 (2C), 31.9 (2C), 29.6 (6C), 29.4 (4C), 29.3 (4C), 26 (2C), 22.6 (2C), 17.9 (2C), 17.6 (2C), 14 (2C); IR (KBr): 2850, 1700, 1600, 1220 cm^{-1}; HRMS (ESI): m/z (M+H)$^+$ calculated for $C_{73}H_{106}O_{15}$: 1223.7611; found: 1223.7614.

5.3. General procedure for the preparation of compounds 19–21

To a mixture of oxa-bridged diacid **9** (200 mg, 0.7 mmol), triethylamine (177 mg, 1.75 mmol) in THF (4 mL) was added 2,4,6-trichlorobenzoyl chloride (350 mg, 1.43 mmol). The reaction mixture was stirred at room temperature for 2 h and resultant solution was then added to a mixture of 2-(4-((4-(dodecyloxy) phenyl)diazenyl)phenoxy)ethanol (685 mg, 1.61 mmol) and DMAP (197 mg, 1.61 mmol) in THF (6 mL). The reaction mixture was stirred at room temperature for 3 h under argon atmosphere. After reaction was completed sodium bicarbonate solution (3 mL) was added followed by distilled water (15 mL). The solution was extracted with ethyl acetate (4×4 mL) and the combined organic layers were washed with distilled water (3×3 mL), brine solution (3 mL) and dried over anhydrous sodium sulfate, filtered and concentrated afforded the crude product, which on purification on silica gel column chromatography using 50% ethyl acetate/hexane afforded **19** (593 mg, 77%).

5.3.1. Compound ***19***. Yellowish glassy solid; mp: 92 °C; R_f (40% ethyl acetate/hexane) 0.40; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.8 (m, 8H), 6.92–6.87 (m, 8H), 4.65–4.6 (m, 2H), 4.47–4.43 (m, 2H), 4.21 (m, 4H), 3.96 (t, J=6.6 Hz, 4H), 3.37 (s, 3H), 3.25 (s, 3H), 2.66–2.64 (m, 2H), 1.77–1.71 (m, 8H), 1.4–1.19 (m, 40H), 0.81 (t, J=6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2 (2C), 161.3 (2C), 160.1 (2C), 147.5 (2C), 146.9 (2C), 124.3 (8C), 114.7 (8C), 110.3, 92.1 (2C), 68.4 (2C), 65.8 (2C), 63.2 (2C), 52.2, 51.5, 41.9 (2C), 31.9 (2C), 29.61 (2C), 29.6 (6C), 29.4 (4C), 29.2 (2C), 26 (2C), 22.6 (2C), 17.9 (2C), 17.6 (2C), 14.1 (2C); IR (KBr): 2850, 1720, 1600, 1500, 1240 cm^{-1}; HRMS (ESI): m/z (M+H)$^+$ calculated for $C_{65}H_{90}N_4O_{11}$: 1103.6684; found: 1103.6681.

5.3.2. Compound ***20***. Yield: 87%; yellowish glassy solid; mp: 62 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J=8.7 Hz, 8H), 7.19–6.89 (m, 8H), 4.44–4.39 (m, 2H), 4.29–4.24 (m, 2H), 4.08 (t, J=4.8 Hz, 4H), 3.94 (t, J=6.6 Hz, 4H), 3.79–3.72 (m, 8H), 3.37 (s, 3H), 3.26 (s, 3H), 2.63–2.61 (m, 2H), 1.75–1.69 (m, 8H), 1.39–1.19 (m, 40H), 0.81 (t, J=6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3 (2C), 161.3 (2C), 160.6 (2C), 147.1 (2C), 146.7 (2C), 124.4 (4C), 124.3 (4C), 114.7 (4C), 114.6 (4C), 110.1, 92 (2C), 69.5 (2C), 68.9 (2C), 68.3 (2C), 67.7 (2C), 63.9 (2C), 52.2, 51.6, 41.9 (2C), 31.9 (2C), 29.6 (8C), 29.3 (4C), 29.2 (2C), 25.9 (2C), 22.7 (2C), 17.9 (2C), 17.5 (2C), 14.1 (2C); IR (KBr): 2850, 1720, 1580, 1440, 1240 cm^{-1}; HRMS (ESI): m/z (M+H)$^+$ calculated for $C_{69}H_{98}N_4O_{13}$: 1191.7209; found: 1191.7202.

5.3.3. Compound ***21***. Yield: 85%; yellowish glassy solid; mp: 64 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J=8.8 Hz, 8H), 6.92 (dd, J=11.5, 8.8 Hz, 8H), 4.38–4.33 (s, 2H), 4.26–4.21 (s, 2H), 4.11 (t, J=4.6 Hz, 4H), 3.93 (t, J=6.4 Hz, 4H), 3.79 (t, J=4.6 Hz, 4H), 3.65–3.57 (m, 12H), 3.37 (s, 3H), 3.27 (s, 3H), 2.64–2.61 (m, 2 H), 1.76–1.69 (m, 8H), 1.39–1.19 (m, 40H), 0.80 (t, J=6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3 (2C), 161.2 (2C), 160.7 (2C), 147 (2C), 146.7 (2C), 124.3 (4C), 124.2 (4C), 114.7 (4C), 114.6 (4C), 110.1, 91.9 (2C), 70.7 (2C), 70.5 (2C), 69.6 (2C), 68.7 (2C), 68.2 (2C), 67.6 (2C), 63.9 (2C), 52.1, 51.6, 41.8 (2C), 31.8 (2C), 29.6 (4C), 29.5 (4C), 29.33 (2C), 29.29 (2C), 29.1 (2C), 25.9 (2C), 22.6 (2C), 17.9 (2C), 17.5 (2C), 14.0 (2C); IR (KBr): 2850, 1720, 1600, 1500, 1240 cm^{-1}; HRMS (ESI): m/z (M+H)$^+$ calculated for $C_{73}H_{106}N_4O_{15}$: 1279.7734; found: 1279.7736.

5.4. General procedure for the preparation of compounds 22–24

To a mixture of oxa-bridged diacid **9** (200 mg, 0.7 mmol), triethylamine (177 mg, 1.75 mmol) in THF (4 mL) was added 2,4,6-trichlorobenzoyl chloride (350 mg, 1.43 mmol). The reaction mixture was stirred at room temperature for 2 h and resultant solution was then added to a mixture of cholesterol (622 mg, 1.61 mmol) and DMAP (197 mg, 1.61 mmol) in THF (8 mL). The reaction mixture was stirred at room temperature for 3 h under argon atmosphere. After reaction was completed sodium bicarbonate solution (3 mL) was added followed by distilled water (15 mL). The solution was extracted with ethyl acetate (4×4 mL) and the combined organic layers were washed with distilled water (3×3 mL), brine solution (3 mL) and dried over anhydrous sodium sulfate, filtered and concentrated afforded the crude product, which on purification on silica gel column chromatography using 8% ethyl acetate/hexane afforded **22** (450 mg, 63%).

5.4.1. Compound ***22***. Colourless solid; mp: 236 °C; R_f (10% ethyl acetate/hexane) 0.50; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.38–5.35 (m, 2H), 4.82–4.73 (m, 2H), 3.46 (s, 3H), 3.36 (s, 3H), 2.68–2.66 (m, 2H), 2.43–2.28 (m, 4H), 2.02–1.94 (m, 4H), 1.88–1.04 (m, 56H), 1.0 (s, 6H), 0.91 (d, J=6.6 Hz, 6H), 0.86 (dd, J=6.6, 1.7 Hz, 12H), 0.67 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9 (2C), 139.6 (2C), 122.9 (2C), 110.1, 91.9 (2C), 75.1 (2C), 56.7 (2C), 56.2 (2C), 52.2, 51.5, 50 (2C), 42.3 (2C), 41.9 (2C), 39.7 (2C), 39.5 (2C), 37.9 (2C), 36.9 (2C), 36.6 (2C), 36.2 (2C), 35.8 (2C), 31.9 (4C), 28.2 (2C), 27.9 (2C), 27.6 (2C), 24.3 (2C), 23.8 (2C), 22.8 (2C), 22.5 (2C), 21 (2C), 19.3 (2C), 18.7 (2C), 18.1 (2C), 17.6 (2C), 11.8 (2C); IR (KBr): 2800, 1740, 1440, 1260 cm^{-1}; HRMS (ESI): m/z (M+H)$^+$ calculated for $C_{67}H_{106}O_7$: 1023.8018; found: 1023.8017.

5.4.2. Compound ***23***. Yield: 90%; colourless solid; mp: 166 °C; R_f (30% ethyl acetate/hexane) 0.40; ^{1}H NMR (400 MHz, $CDCl_3$):

δ 5.34–5.33 (m, 2H), 4.47–4.42 (m, 2H), 4.32–4.27 (m, 2H), 3.74–3.71 (m, 4H), 3.59 (s, 8H), 3.45 (s, 3H), 3.53 (s, 3H), 3.18–3.12 (m, 2H), 2.72–2.69 (m, 2H), 2.37–2.33 (m, 2H), 2.22–2.16 (m, 2H), 2.02–1.02 (m, 60H), 0.99 (s, 6H), 0.91 (d, *J*=6.6 Hz, 6H), 0.86 (dd, *J*=6.6, 1.72 Hz, 12H), 0.67 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2 (2C), 140.9 (2C), 121.5 (2C), 110.1, 92 (2C), 79.5 (2C), 70.8 (2C), 68.7 (2C), 67.3 (2C), 63.9 (2C), 56.8 (2C), 56.2 (2C), 52.1, 51.5, 50.2 (2C), 42.3 (2C), 41.9 (2C), 39.8 (2C), 39.5 (2C), 39.1 (2C), 37.2 (2C), 39.8 (2C), 36.2 (2C), 35.7 (2C), 31.9 (4C), 28.4 (2C), 28.2 (2C), 27.9 (2C), 24.3 (2C), 23.8 (2C), 22.7 (2C), 22.5 (2C), 21.1 (2C), 19.3 (2C), 18.7 (2C), 18 (2C), 17.6 (2C), 11.8 (2C); IR (Neat): 2800, 1720, 1440, 1240 cm^{-1}; HRMS (ESI): *m*/*z* $(M+H)^+$ calculated for $C_{75}H_{122}O_{11}$: 1199.9066; found: 1199.9064.

5.4.3. Compound ***24***. Yield: 91%. Thick liquid, R_f (30% ethyl acetate/hexane) 0.40; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.31–5.30 (m, 2H), 4.34–4.39 (m, 2H), 4.29–4.24 (m, 2H), 3.70–3.66 (m, 4H), 3.59 (s, 16H), 3.42 (s, 3H), 3.31 (s, 3H), 3.17–3.1 (m, 2H), 2.68–2.66 (m, 2H), 2.36–2.31 (m, 2H), 2.21–2.17 (m, 2H), 1.99–0.98 (m, 60H), 0.96 (s, 6H), 0.88 (d, *J*=6.6 Hz, 6H), 0.83 (dd, *J*=6.6, 1.7 Hz, 12H), 0.64 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3 (2C), 140.9 (2C), 121.5 (2C), 110.2, 92 (2C), 79.5 (2C), 70.9 (2C), 70.6 (4C), 68.7 (2C), 67.3 (2C), 63.9 (2C), 56.8 (2C), 56.2 (2C), 52.1, 51.6, 50.2 (2C), 42.3 (2C), 41.9 (2C), 39.8 (2C), 39.5 (2C), 39.1 (2C), 37.3 (2C), 36.9 (2C), 36.2 (2C), 35.8 (2C), 31.9 (4C), 28.4 (2C), 28.2 (2C), 27.9 (2C), 24.3 (2C), 23.8 (2C), 22.8 (2C), 22.5 (2C), 21.1 (2C), 19.4 (2C), 18.7 (2C), 18 (2C), 17.6 (2C), 11.9 (2C); IR (KBr): 2850, 1720, 1440, 1220 cm^{-1}; HRMS (ESI): *m*/*z* $(M+H)^+$ calculated for $C_{79}H_{130}O_{13}$: 1287.9590; found: 1287.9594.

5.4.4. Compound ***12***. Bis-oxa-bridged tetra-ester (300 mg, 0.552 mmol) in dry dichloromethane (5 mL) was added DIBAL-H (0.88 g, 4.4 mL, 20 wt % in toluene) at −78 °C under argon atmosphere. Reaction mixture was warmed to room temperature and stirred for 3 h. Reaction was quenched using triethylamine/water (1:1) at −78 °C and slowly brought to room temperature. A white solid separated, was filtered through small pad of Celite, washed with 10% MeOH/$CHCl_3$. The filtrate was concentrated under reduced pressure afforded 235 mg of oxa-bridged tetrol. The crude tetrol in dry dichloromethane (3 mL) was added pyridine (1 mL) followed by acetic anhydride (1.2 mL) at 0–5 °C. Reaction mixture was stirred at room temperature for 9 h and quenched with water (5 mL) and the solution was extracted with dichloromethane (4×3 mL), combined organic layers were washed with 1% HCl (2×2 mL), water (2×2 mL), brine solution (2 mL) and dried over anhydrous sodium sulfate, filtered and concentrated afforded the crude product, which on purification on silica gel column chromatography using 40–50% ethyl acetate/hexane afforded the compound **12** (237 mg, 72%). Colourless solid; mp: 208–210 °C; R_f (50% ethyl acetate/hexane) 0.50; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.3 (d, *J*=12.4 Hz, 4H), 4.19 (d, *J*=12.4 Hz, 4H), 3.37 (s, 6H), 3.2 (s, 6H), 2.37 (dd, *J*=8.0, 4.7 Hz, 4H), 2.04 (s, 12H), 1.45–1.28 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2 (4C), 105.8 (2C), 92.6 (4C), 58.3 (4C), 51.8 (2C), 51.4 (2C), 38.0 (4C), 20.7 (4C), 17.1 (2C); HRMS (ESI): *m*/*z* $(M-H)^-$ calculated for $C_{28}H_{40}O_{14}$: 599.2339; found: 599.2345.

5.4.5. Compound ***25***. To a mixture of 2-(4′-(dodecyloxy)biphenyl-4-yloxy)acetic acid (107 mg, 0.26 mmol), triethylamine (39 mg, 0.39 mmol) in THF (2 mL) was added 2,4,6-trichlorobenzoyl chloride (70 mg, 0.29 mmol). The reaction mixture was stirred at room temperature for 2 h and resultant solution was then added to a mixture of tetrol **10** (25 mg, 0.058 mmol) and DMAP (32 mg, 0.26 mmol) in THF (3 mL). The reaction mixture was stirred at room temperature for 8 h under argon atmosphere. After reaction was completed sodium bicarbonate solution (3 mL) was added followed by distilled water (10 mL). The organics were extracted with ethyl acetate (4×4 mL) and the combined organics were washed with distilled water (3×3 mL), brine solution (3 mL) and dried over anhydrous sodium sulfate, filtered and concentrated afforded the crude product, which on purification on silica gel column chromatography using 25% ethyl acetate/hexane afforded the compound **25** (46 mg, 37%). Colourless solid; mp: 165 °C; R_f (30% ethyl acetate/hexane) 0.40; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.34 (m, 16H), 6.88–6.82 (m, 16H), 4.58 (s, 8H), 4.29 (s, 8H), 3.88 (t, *J*=6.6 Hz, 8H), 3.24 (s, 6H), 3.04 (s, 6H), 2.17–2.14 (m, 4H), 1.74–1.67 (m, 4H), 1.39–1.16 (m, 80H), 0.81 (t, *J*=6.8 Hz, 12H);^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3 (4C), 158.4 (4C), 156.6 (4C), 134.6 (4C), 132.7 (4C), 127.8 (8C), 127.7 (8C), 114.9 (8C), 114.8 (8C), 105.8 (2C), 92.5 (4C), 68 (4C), 65.1 (4C), 58.8 (4C), 51.8 (2C), 51.4 (2C), 37.9 (4C), 31.9 (4C), 29.65 (4C), 29.62 (8C), 29.59 (4C), 29.57 (4C), 29.4 (4C), 29.3 (4C), 29.27 (4C), 26 (4C), 22.7 (2C), 14.1 (4C); IR (KBr): 2800, 1720, 1600, 1440,1220 cm^{-1}; MALDI-TOF: *m*/*z* $(M+Na)^+$ calculated for $C_{124}H_{168}O_{22}$: 2032.193; found: 2032.086.

5.4.6. Compound ***26***. To a mixture of 10-(biphenyl-4-yloxy)decanoic acid (53 mg, 0.156 mmol), triethylamine (24 mg, 0.24 mmol) in THF (2 mL) was added 2,4,6-trichlorobenzoyl chloride (42 mg, 0.172 mmol). The reaction mixture was stirred at room temperature for 2 h and resultant solution was then added to a mixture of tetrol **10** (15 mg, 0.035 mmol) and DMAP (19 mg, 0.155 mmol) in THF (3 mL). The reaction mixture was stirred at room temperature for 8 h under argon atmosphere. After reaction was completed, sodium bicarbonate solution (3 mL) was added followed by distilled water (10 mL). The solution was extracted with ethyl acetate (4×4 mL) and the combined organic layers were washed with distilled water (3×3 mL), brine solution (3 mL) and dried over anhydrous sodium sulfate, filtered and concentrated afforded the crude product, which on purification on silica gel column chromatography using 30% ethyl acetate/hexane afforded the compound **26** (46 mg, 77%). Colourless solid; mp: 78 °C; R_f (25% ethyl acetate/hexane) 0.60; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.41 (m, 16H), 7.34–7.3 (m, 8H), 7.24–7.19 (m, 4H), 6.89–6.86 (8H), 4.28 (d, *J*=12.4 Hz, 4H), 4.18 (d, *J*=12.4 Hz, 4H), 3.9 (t, *J*=6.6 Hz, 8H), 3.31 (s, 6H), 3.12 (s, 6H), 2.35–2.28 (m, 4H), 2.24 (t, *J*=7.5 Hz, 8H), 1.75–1.68 (m, 8H), 1.55–1.52 (m, 8H), 1.42–1.35 (m, 8H), 1.23–1.18 (m, 36H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173 (4C), 158.8 (4C), 140.9 (4C), 133.6, (4C), 128.8 (8C), 128.2 (8C), 126.8 (8C), 126.7 (8C), 114.8 (8C), 105.9 (2C), 92.8 (4C), 68.1 (4C), 58.3 (4C), 51.9 (2C), 51.6 (2C), 38.3 (4C), 34.1 (4C), 29.53 (4C), 29.47 (4C), 29.4 (4C), 29.3 (2C), 29.2 (2C), 26.2 (4C), 24.9 (4C), 17.2 (2C); IR (KBr): 2800, 1720, 1600, 1440 cm^{-1}; MALDI-TOF: *m*/*z* $(M+Na)^+$ calculated for $C_{108}H_{136}O_{18}$: 1743.963; found: 1743.891.

5.4.7. Compound ***27***. To a mixture of cholesterol-derived acid (77 mg, 0.158 mmol), triethylamine (24 mg, 0.24 mmol) in THF (2 mL) was added 2,4,6-trichlorobenzoyl chloride (42 mg, 0.172 mmol). The reaction mixture was stirred at room temperature for 2 h and resultant solution was then added to a mixture of tetrol **10** (15 mg, 0.035 mmol) and DMAP (19 mg, 0.155 mmol) in THF (3 mL). The reaction mixture was stirred at room temperature for 8 h under argon atmosphere. After reaction was completed sodium bicarbonate solution (3 mL) was added followed by distilled water (15 mL). The solution was extracted with ethyl acetate (4×4 mL) and the combined organic layers were washed with distilled water (3×3 mL), brine solution (3 mL) and dried over anhydrous sodium sulfate, filtered and concentrated afforded the crude product, which on purification on silica gel column chromatography using 20–30% ethyl acetate/hexane afforded the compound **27** (61 mg, 76%). Colourless solid; mp: 180 °C; R_f (40% ethyl acetate/hexane) 0.60; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.37–5.36 (m, 4H), 4.61–4.58 (m, 4H), 4.37 (d, *J*=12.2 Hz, 4H), 4.23 (d, *J*=12.2 Hz, 4H), 3.39 (s, 6H), 3.23 (s, 6H), 2.63–2.59 (m, 16H), 2.41–2.29 (m, 8H), 2.02–1.04 (m, 112H), 1.01 (s, 12H), 0.91 (d, *J*=6.6 Hz, 12H), 0.86 (dd, *J*=6.6, 1.7 Hz,

24H), 0.68 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5 (4C), 171.4 (4C), 139.6 (4C), 122.7 (4C),105.9 (2C), 92.7 (4C), 74.4 (4C), 58.5 (4C), 56.8 (4C), 56.3 (4C), 51.8 (2C), 51.5 (2C), 50.1 (4C), 42.4 (4C), 39.8 (4C),39.5 (4C), 38.1 (4C), 37.0 (4C), 36.6 (4C), 36.2 (4C), 35.8 (4C), 31.9 (8C), 29.3 (4C), 29 (4C), 28.2 (4C), 27.99 (4C), 27.8 (8C), 24.3 (4C), 23.9 (4C), 22.8 (4C), 22.5 (4C), 21.1 (4C), 19.3 (4C), 18.7 (4C), 17.1 (2C), 11.9 (4C); IR (KBr): 2800, 1740, 1720, 1440, 1260 cm^{-1}; MALDI-TOF: *m*/*z* $(M+Na)^+$ calculated for $C_{144}H_{224}O_{22}$: 2328.631; found: 2328.492.

Acknowledgements

We thank the Department of Science and Technology (DST), New Delhi for financial assistance. F.A.K. acknowledges the DST for a Swarnajayanti Fellowship. K.P. thank CSIR, New Delhi for fellowship. B.D. thank the CNRS and the University of Styrasbourg for support.

Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.09.003.

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