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Syntheses and Mesogenic Properties of Dimers and Trimers Consisting of Triphenylene Donor and Anthraquinone Acceptor

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The synthesis and liquid crystalline properties of new dimers with triphenylene donor (D) core tethered via a flexible spacer to a monofunctionalized anthraquinone acceptor (A) core, ***D-A****, are reported. These dimers have hydroxyl (****D-A(OH)****) or acetyloxy (****D-A(OAc)****) functional group. The linear trimers,* ***D-A-D****, are also reported here. The chemical structures of these dimers and trimers are characterized by spectroscopic and spectrometric analysis. The liquid crystalline properties are investigated by polarizing optical microscope (POM) and differential scanning calorimetry (DSC). The dimers* ***D-A(OH)*** *having the spacer length similar to peripheral alkoxy chains exhibit the nematic (N) phase, whereas dimers* ***D-A(OH)*** *and* ***D-A(OAc)*** *having longer spacer length compared with peripheral alkoxy chains exhibit the columnar (Col) phase. The trimers exhibit N or Col mesophases, as confirmed by X-ray diffraction (XRD) studies, according to the similar rule as in D-A. Thus the spacer length and functional group have more influence on molecular self-assembly to exhibit the liquid crystalline properties. It is noted that some of these dimers and trimers show N or Col phase at room temperature. To the best of our knowledge, this is the first for molecules with non-branched but normal peripheral chains.*

Keywords Anthraquinone; dimers; discotic liquid crystals; oligomers; triphenylene

1. Introduction

Charge transfer (CT) complexes or donor–acceptor (D-A) twins, oligomers, and dendrimer molecules are especially attractive because of their unique liquid crystalline properties which show great promise in electronic devices [1]. The numerous dimers with variety of entities [2] have been developed. Since inter- or intramolecular interactions have large effect on the mesophase morphology [3,4], such combinations

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Address correspondence to Hideo Takezoe, Department of Organic and Polymeric Materials, O-okyama 2-12-1, Meguro-ku, Tokyo 152-8552, Japan. E-mail: takezoe.h.aa@m.titech.ac.jp are incorporated into a self-assembled system. A variety of dimers, in which a donor is connected to an acceptor via a flexible spacer, are reported [5]. Only the non-mesogenic 2,4,7-trinitrofluoren-9-one (TNF) as an electron acceptor with discotic liquid crystals (DLCs) [6] in the preparation of dimers is well recognized. The novel mesomorphic behavior of dimers based on triphenylene [7a], pentaalkynylbenzene [7b], pyrene [7c], hexabenzocorene [7d], etc. are also reported. Substitution of electron donating functional group or electron withdrawing group at appropriate locations in an aromatic moiety can change its overall electronegativity. This leads to π-delocalized aromatic units with distinct donor and acceptor properties, which may lead to partial charge transfer when donor and acceptor are combined [8]. Prasad and Varshney [9] have reported, for the first time, the synthesis of non-symmetrical dimers consisting of a spacer chain with ether linkage at one end and an ester at the other end. (Here onwards we refer to this combination of linkage as "ether–ester" linkage, for the sake of simplicity.) The dimers exhibited the poly-mesomorphism. As a continuation of this work, we have designed and synthesized two more series of dimers bearing a pentakis(alkoxy)triphenylene [10] donor which is connected to a monofunctionalized anthraquinone [11] acceptor. The synthesis and liquid crystalline properties of these dimers are described.

Discotic trimers are usually star-shaped or linear. The remarkable optical properties of non-symmetrical linear trimer bearing electron-rich triphenylene and electron-deficient TNF covalently linked through azobenzene have been reported [12]. These results promoted the interest of chemists to synthesize organic molecules that can enhance the liquid crystalline properties of such systems. Synthesis of star-shaped discotic trimers is somewhat simple compared to the linear ones. This could be the reason why only a very few discotic linear trimers are known in the literature [13]. Recently, the highest ever charge carrier mobility in triphenylene system based on star-shaped trimer has been reported [14]. These molecules can enhance electron conductivity and are regarded as "organic metals." Very recently, symmetric linear trimers consisting of triphenylene (TP) and anthraquinone (AQ) with ether–ether linkages were synthesized using microwave-assisted method [15]. We have designed and synthesized similar linear trimer type molecules. TP and AQ cores have also been used as donor and acceptor, respectively. But the molecules are different from the previous one [15]; i.e., they have different asymmetric chain length with ether–ester linkage and are prepared by conventional heating. The synthesis and liquid crystalline properties of these trimers are also discussed here.

2. Result and Discussion

Specific molecular interactions, such as hydrogen bonding, D-A complexation, dipole–dipole interactions, etc. are utilized for the self-organization of molecules in liquid crystal (LC) system. Based on these factors, we designed and synthesized two series of dimers consisting of hydroxyl and acetyloxy functional groups, which are referred to as **D-A(OH)** and **D-A(OAc)**, respectively. Here, in the case of **D-A(OH)** and **D-A(OAc)**, TP moiety is linked to an AQ moiety via an alkyl chain with ether–ester linkage, as shown by circles in Fig. 1. To study the effect of linking functional group, trimers referred to as **D-A-D** are also synthesized, where two donor TP molecules are linked with acceptor AQ molecule by an ether–ether or ester–ester linkage. The chemical structures of new dimer and trimer molecules are shown in Fig. 1.

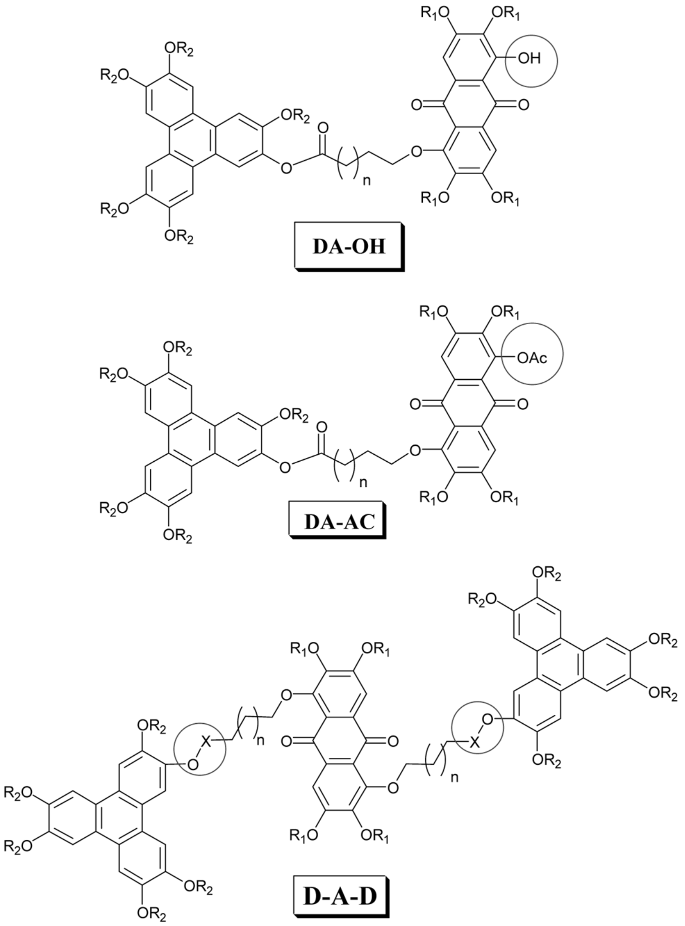
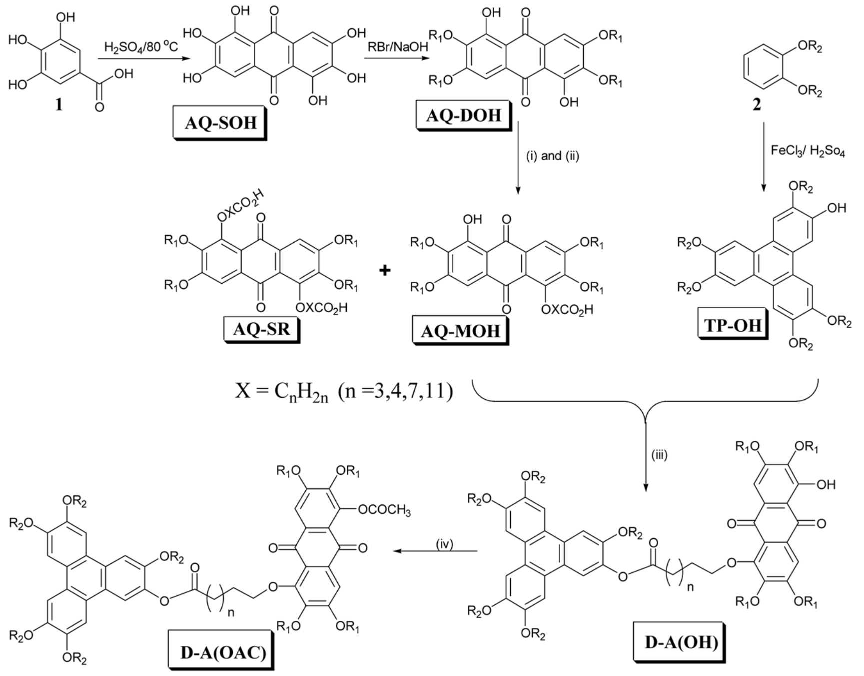


Figure 1. Chemical structures of the compounds synthesized.

A convergent strategy was used to synthesize the non-symmetrical oligomers. The monohydroxypentakis(alkoxy)TP (**TP-OH**) and dihydroxytetrakis(alkoxy)AQ (**AQ-DOH**) entity are key intermediates to prepare these dimers and trimers. The **TP-OH** was prepared by oxidative trimerization of dialkoxybenzene (**2**) in the presence of excess conc. H_2SO_4 [10]. The **AQ-DOH** was prepared by gallic acid and selective alkylation [16,17]. The synthesis route of dimers is shown in Scheme 1.

The **AQ-DOH** was alkylated with ethyl *n*-bromoalkanoate in the presence of K_2CO_3 as a base. The ethyl *n*-bromoalkanoate was prepared by commercially available *n*-bromoalkanoic acid. The TLC of crude product showed the two product formations in 1:1 ratio. Both the products were separated by column chromatography technique and were deprotected in the presence of base. The chemical structures of the deprotected molecules were confirmed by spectral data that concluded the 8,8′-(2,3,6,7-tetrakis(alkoxy)-9,10-dioxo-9,10-dihydroanthracene-1,5-diyl)bis(oxy) dialkanoic acid (**AQ-SR**) and ω-oxyalkanyolmonohydroxytetrakis(alkoxy)AQ (**AQ-MOH**) in 55% yield. The **D-A(OH)** series dimers were synthesized by 1,3-dicyclohexylcarbodiimide (**DCC**) coupling of **TP-OH** and **AQ-MOH** in 46% yield



(1): $R_1 = R_2 = C_4H_9$; n = 1 ; (2): $R_1 = R_2 = C_5H_{11}$; n = 2
(3): $R_1 = R_2 = C_8H_{17}$; n = 5 ; (4): $R_1 = R_2 = C_4H_9$; n = 5
(5): $R_1 = R_2 = C_6H_{13}$; n = 9 ; (6): $R_1 = R_2 = C_8H_{17}$; n = 9
(7): $R_1 = R_2 = C_7H_{15}$; n = 5 ; (8): $R_1 = C_8H_{17}$; $R_2 = C_4H_9$; n = 5

[a]Key: (i) $BrC_xH_{2x}COOEt$ /K_2CO_3 / DMF / 100 °C /24h. (ii) KOH / MeOH /100 °C / 5h. (iii) DCC /DMAP /CH_2Cl_2 /r.t/ 48h. (iv) Py./ Acetic anhydride / 80 °C / 15h.

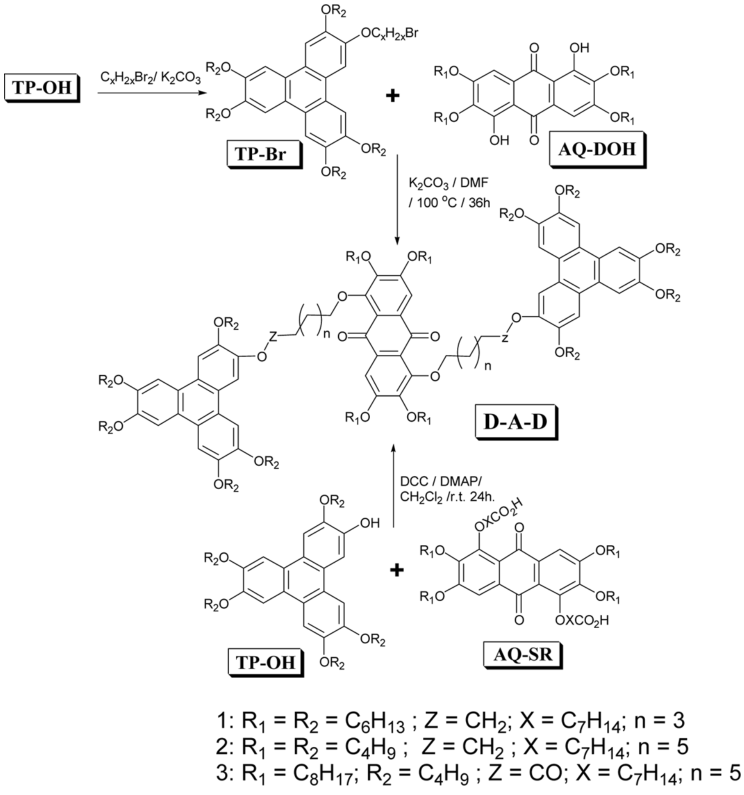
Scheme 1. Synthesis of monofunctionalized **D-A** dimers.

which was purified by column chromatography. The selected derivatives of the **D-A(OAc)** dimer series were prepared by acetylating of **D-A(OH)** dimer in the presence of acetic anhydride and pyridine (Scheme 1). The trimer series are synthesized by conventional synthetic methods as outlined in Scheme 2.

The required intermediate of ether–ether derivative β-(ω-bromoalkoxy)pentakis (alkoxy)TP was prepared by alkylation of **TP-OH** with the excess of α,ω-dibromoalkane in the presence of K_2CO_3 under the conventional heating. The ether–ether trimer derivatives **D-A-D (1,2)** are prepared by alkylation of **AQ-DOH** with β-(ω-bromoalkoxy)pentakis(alkoxy)TP (**TP-Br**) and ester–ester derivative **D-A-D (3)** was obtained by coupling **TP-OH** with **AQ-SR** in the presence of **DCC** and 4-(*N*,*N*,-dimethylamino)pyridine (**DMAP**) as catalyst. All these compounds were characterized by ^{1}H NMR, ^{13}C NMR, elemental analysis, IR spectra, and mass spectroscopy.

Mesomorphic Behavior

The mesomorphic behavior of these dimers and trimers were examined by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC) and



Scheme 2. Synthesis of **D-A-D** trimers by conventional methods.

columnar phase was confirmed by X-ray diffraction (XRD) studies. The phase transition data and *d* spacing data are summarized in Table 1.

The crystal to mesophase transition was found to be irreversible. On cooling, most of mesophases supercooled to room temperature (RT) and only one of the derivatives of the series **D-A(OH)(1)** crystallized at RT. Other derivatives did not show Cr–M transition. Dimer of series **D-A(OH)** having identical peripheral and linking spacer length exhibit the N mesophase, i.e., **DA-H(1)**, **(3)**, and **(7)**. Compound **D-A(OH)(1)** shows the N phase that clears to isotropic liquid at 121.9°C. On cooling, schlieren texture of the N phase (Fig. 2(a)) appears at 118.7°C. This N phase is transformed to crystalline state at 102.4°C. The next higher homologues **D-A(OH)(2)** did not exhibits mesophase. On increasing the peripheral alkoxy chains to eight carbons, derivative **D-A(OH)(3)** exhibits the N phase at RT that clears at 43.8°C to isotropic liquid. On cooling, the N phase appeared at 42.7°C and did not change till ambient temperature (RT, 25°C). These transitions were confirmed by DSC, as shown in Fig. 3. A classical texture of the N phase appeared on cooling from the isotropic liquid as shown in Fig. 2(b). Similar texture is seen in **D-A(OH)(7)** derivative also (not shown). Increasing the spacer length compared with the peripheral alkoxy chain length, **D-A(OH)(4~6)** exhibit Col mesophase (Fig. 2(c)) over a wide thermal range. The texture of Col phase is very similar to the known texture for the $\mathrm{Col_h}$ mesophase shown by several well-characterized discotic liquid crystals [7]. **D-A(OH)(5)** transforms to the glassy state at 64.5°C. However, compound

Table 1. Thermal properties and X-ray results of **DA-OH**, **DA-AC** dimer series, and **D-A-D** trimer series

Compound	Thermal behaviour[a] Heating scan/Cooling scan	X-ray results (Å) $d_{obs}/d_{inter}/d_{intra}$
D-A(OH) series		
(1)	Cr 121.9 (18.2) I/I 118.7 (2.3) N 102.4 (4.2) Cr	
(2)	ss 56 (1.8) I	
(3)	N 43.8 (0.9) I/I 42.7 (0.4) N	
(4)	Col_h 165.5 (19.6) I/I 163.4 (19.3) Col_h	15.8/18.3/3.9
(5)	Col 117 (5.2) I/I 110.7 (3.6) Col 64.5 Col_g	
(6)	Col 80 (0.9) I/I 72 (2.2) Col	
(7)	N 42.2 (1.1) I/I 41 (0.3) N	
(8)	ss 61 (39.2) I	
D-A(OAc) series		
(3)	ss 66 (5.3) I	
(5)	Col 91 (2.2) I/I 85 (3.8) Col	
(7)	ss 62 (3.8) I	
(8)[b]	Cr 106 I/I 95 M_x	
D-A-D-Series		
(1)	Cr 75.0 (18.3) I/I 58.3 (17.6) Cr	
(2)	Col_h 103.8 (12.7) I/I 100.5 (15.1) Col_h	16.1/18.6/3.4
(3)	N_x 80.3 (1.3) N 90.3 (6.8) I/I 88.9 (7.2) N 72 (0.6) N	

[a] Phase transition temperatures (°C) and enthalpies ($kJmol^{-1}$) in parentheses.
[b] Transition obtained by POM; N = nematic; Col = columnar; I = isotropic; g = glassy state; ss = semisolid; N_x = unknown nematic phase; M_x = unknown phase.

D-A(OH)(6) does not show the metastable glassy state at RT. Usually, compounds with longer spacer chains have a shorter lifetime of glassy state, and rapidly crystallization occurs. The **D-A(OH)(8)** derivative is nonliquid crystalline in which the peripheral alkoxy chain of the acceptor moiety is shorter than the donor moiety and the spacer length.

The selected derivatives (3, 5, 7, and 8) of the **D-A(OAc)** series were also prepared. We found that derivative **D-A(OAc)(5)** is mesomorphic in which the linking spacer length is double of the peripheral alkoxy chains. On heating, the Col phase was converted to the isotropic liquid at 91°C and on cooling, the Col phase appeared at 85°C. Other two derivatives **D-A(OAc)(3** and **7)** with similar linking spacer length to the peripheral alkoxy chain lengths are non-mesogenic. It is worth mentioning that compound **D-A(OAc)(8)** having the spacer length double of the peripheral alkoxy chains of donor and similar to those of the acceptor was found to be transformed to an unknown phase, designated as M_x here, on cooling at 95°C, although it was difficult to detect even by POM observation. DSC thermogram did not show any transition either. This complexity may occur due to the functional group. Here we found that the hydroxyl functional group has a considerable effect on molecular morphology and transition temperatures. The self-organization of non-conventional type of molecules such as dimers particularly arises due to its overall electronegativity of the compound and should give rise to molecular interaction to form the liquid crystalline phases. Thus, non-symmetrical dimer may retain the mesomorphic behavior of the monomer and/or exhibit novel mesomorphic behavior. This could

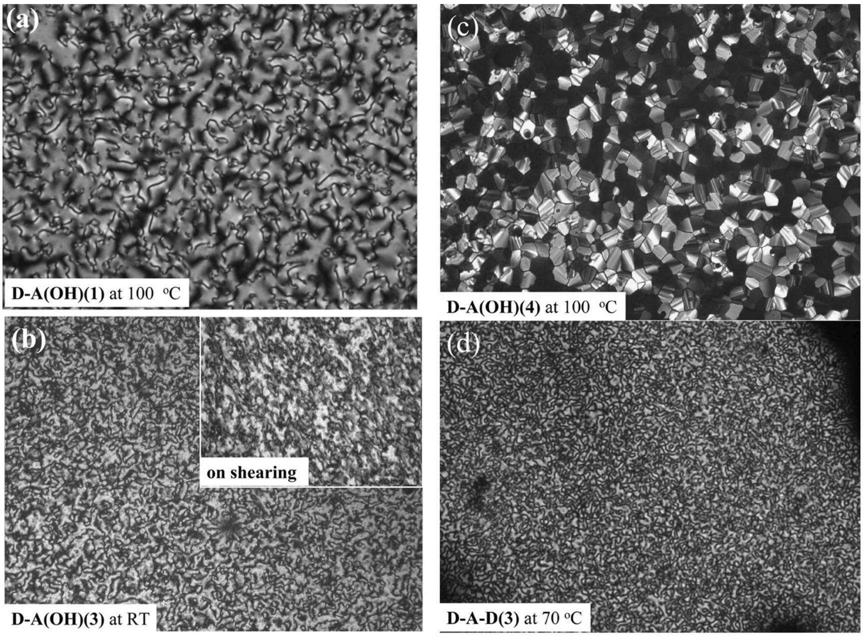


Figure 2. Observed textures in mesophases on cooling from isotropic liquid: (a) nematic phase of **D-A(OH)(1)** at 100°C; (b) nematic phase of **D-A(OH)(3)** at RT; the inset shows the sheared nematic texture at RT; (c) columnar phase of **D-A(OH)(4)** at 100°C; (d) unidentified N_x phase of **D-A-D(3)** at 70°C.

be the reason why these derivatives exhibit the nematic, columnar, and non-liquid crystalline phases [18].

The trimer **D-A-D(1)** with similar spacer length compared with the peripheral chain lengths is non-liquid crystalline. **D-A-D(2)** with longer spacer length than

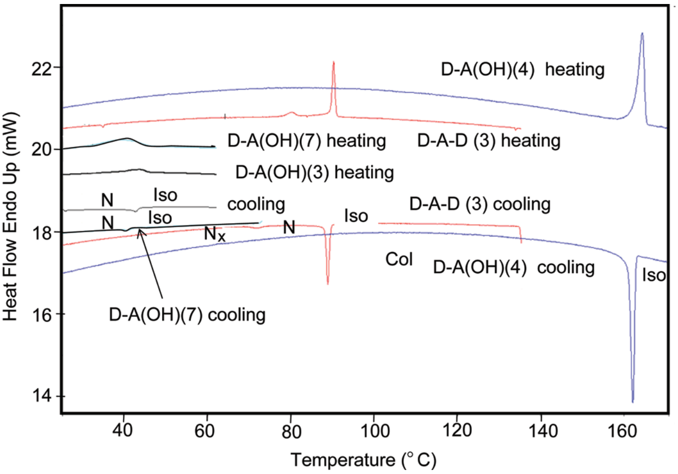


Figure 3. DSC thermograms of **D-A(OH)**, **D-A(OAc)**, and **D-A-D** series of molecules exhibiting the mesophase at RT.

the peripheral alkoxy chain lengths shows the Col mesophase. On cooling, Col mesophase is stabilized down to RT and did not show any sign of crystallization on keeping for a long period, but the mesophase appeared to be transformed into glassy state. To our surprise, we found a large latent heat value ($\Delta H = 6.8\,kJmol^{-1}$) at the transition N-I at 90.3°C in the derivative **D-A-D(3)** with different peripheral alkoxy chains of triphenylene and anthraquinone. This is a strong indication for a locally highly ordered material. The large latent heat ($5\,kJmol^{-1}$) is reported for the associated N phases such as, N_L(nematic lateral, in which principle unit is an aggregate of molecules rather than a single mesogen as in N_D phase and aggregate in all three directions) of discotic dimers by Picken et al. [19]. Further, study is required to confirm the nature of these nematic mesophases. The derivative **D-A-D(3)** shows a weak transition in DSC thermograms (Fig. 3) at 80.3°C ($\Delta H = 1.3$ $kJmol^{-1}$). As shown in Fig. 2(d), schlieren texture is clearly observed in the mesophase at 70°C. Hence we assigned it to nematic, but not identified yet, so we designated as N_x. Further cooling scan did not show the glass transition. The transition data of **D-A-D** trimer series are summarized in Table 1. The efforts were not made to see transition below the RT because of the instrument limitations.

X-Ray Study

To determine the intercolumnar and intracolumnar disc distances in the Col phase, X-ray study was carried out on the **D-A(OH)(4)** and **D-A-D(2)** derivatives. Figure 4 shows a representative 2D diffraction pattern and 1D intensity vs. 2θ profile for the compound **D-A(OH)(4)**. The observed d-spacing (d_{obs}) of the sharp reflection in the small-angle region is 15.83 Å. Although an additional peak corresponding to $d_{obs}/\sqrt{3}$ cannot be observed, we can safely assign the hexagonal columnar phase by referring the previous work [15]. The lack of additional peaks may be due to the disorder of the mesophase as previously reported [7]. The derived intercolumnar

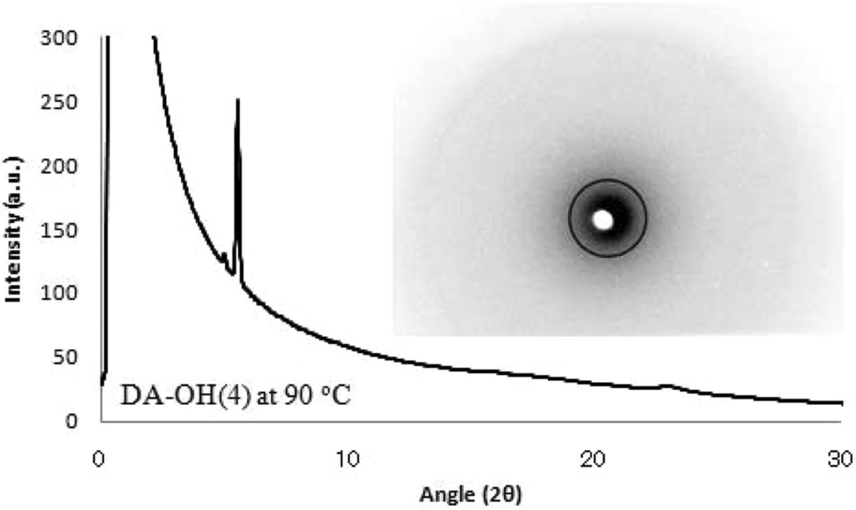


Figure 4. Image plate and intensity vs. 2θ profile of Col_h phase of the dimer **D-A(OH)(4)** at 90°C.

distance for the observed *d*-spacing is (lattice parameter or d_{inter}) 18.29 Å, which approximately agrees with the average monomer size. In the wide-angle region at least one diffuse reflection was observed at about $2\theta = 22.5^{o}$. This is due to the intracolumnar distance (stacking distance) (d_{intra}) of about 3.9 Å. For unoriented samples, we did not observe any additional small angle peaks for the formation of a superlattice arising from the ideal top-on-top stacking of the dimer molecules, suggesting the formation of donor and acceptor double network/cables. Therefore, it was concluded that the triphenylene and anthraquinone monomers arrange themselves statistically to form a columnar hexagonal phase. For the ester linked compound, the increased intermolecular distance along a column is very likely due to the necessary non-planarity of the carboxyl group with respect to the triphenylene. This feature has been observed by Billard et al. [20] for a homologues series of ester derivatives of anthraquinones. However, no sharp ring is visible in the region of the diffuse halo, indicating that the discs are irregularly spaced. A large distance between core-core (3.9 Å) is also observed in the case of anthraquinone dimer (3.46 Å) [11b], the difference is small. This might be accounted for with a twisted packing of the molecules along the column. A similar XRD pattern was obtained in **D-A-D(2)** derivative which shows a sharp reflection in low-angle region (d_{obs} 16.1 Å), indicating a 2D columnar lattice. The *d* spacings are given in Table 1.

3. Experimental

3.1. *General*

Materials: The CH_2Cl_2 (over CaH, under N_2) was distilled prior use. DMF was dried over 4 Å molecular sieves. Unless otherwise noted, reagents were obtained commercially available and used as such without further purification.

Techniques: Column chromatographic (CC) separations were performed at atmospheric pressure using silica gel (70–230 and 200–400 mesh). Analytical thin-layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel 60, F_{254}). Elemental analyses were recorded on a EUROVECTOR 3000 series using acetanilide as standard. ^1H and ^{13}C NMR spectra were recorded on a 200 MHz (^1H, 200 MHz) or 400 MHz (^1H, 400 MHz, ^{13}C, 100 MHz) on Bruker NMR spectrometer in $CDCl_3$. All chemical shifts are reported in parts per million downfield from internal tetramethylsilane $CDCl_3$ ($\delta = 7.26$) for ^1H and ($\delta = 77.0$) for ^{13}C NMR spectra. The *J* values are given in Hz. Infrared spectra (FT-IR) were obtained using Perkin Elmer 1000 series spectrometer. The sample was cast from CH_2Cl_2 solution onto a KBr window. The matrix-assisted laser desorption time-of-flight mass spectrometer (MALDI-TOF MS) was obtained on a Kratos PC Axima CFR V2.3.5 spectrometer using sodiumtrifluoroacetate and anthraline as matrix and JEOL JMS-600H spectrometer in FAB^+ mode using 3-nitrobenzylalcohol (NBA) as matrix.

Liquid-crystalline properties: Transition temperatures were measured using differential scanning calorimetry (DSC-7 or Diamond Perkin-Elmer). Peak temperatures observed in the heating and cooling runs at the rate of $5^{\circ}C\,min^{-1}$ are reported. A polarizing optical microscope (Leica DMLP or Olympous BX51) equipped with a digital camera and Mettler FP82HT hot stage were used for visual observations.

XRD data was obtained by Rigaku RU-200 X-ray system (CuKα) with temperature control unit.

3.2. *Synthesis*

3.2.1. *General Procedure for the Preparation of Intermediates of Anthraquinone and Triphenylene (**AQ-MOH**, **AQ-SR** and **TP-OH**).* The compounds **AQ-SOH** and **AQ-DOH** were synthesized by a reported method. The compound **TP-OH** was prepared by oxidative trimerization of dialkoxybenzene (**2**) by $FeCl_3$ as a byproduct in >35% yield. A stirred mixture of **AQ-DOH** (0.2 mmol), ethyl-α, ω-bromoalkanoate (0.24 mmol), and anhydrous K_2CO_3 (0.4 mmol) in dry DMF was heated (80°C) for 24 h under the anhydrous condition. Filtered the K_2CO_3 and the filtrate was extracted with CH_2Cl_2, washed with distilled water, dried over anhydrous sodium sulphate, and concentrated under vacuum. The residue refluxed with KOH (0.4 mmol) in aqueous methanol for 5 h. The cooled solution was carefully poured into the ice cold aq. HCl, extracted with CH_2Cl_2 and dried over anhydrous sodium sulphate. The solvent was evaporated. The product was purified by column chromatography (CC) over silica gel (60–120 mesh) eluting CH_2Cl_2/hexane. Compound **AQ-MOH** or **AQ-SR** as orange/yellow solid or semisolid in 60–50% overall yield was obtained.

AQ-MOH (1): ν_{max}/cm^{-1}: 2959, 2875, 1709, 1661, 1632, 1572, 1427, 1319, 1282, 1132; **^{1}H NMR**: δ 12.6 (s, 1 H), 7.6 (s, 1 H), 7.4 (s, 1 H), 4.1 (m, 12 H), 2.8 (t, 2 H, $J = 7.2$), 2.2 (m, 2 H), 1.9 (m, 6 H), 1.5 (m, 8 H), 0.9 (m, 12 H); MS m/z: 614 ($M^+ + 1$). **AQ-MOH (2):** ν_{max}/cm^{-1}: 3435 (w), 2953, 2871, 1710, 1662, 1573, 1426, 1322, 1283, 1134; **^{1}H NMR**: δ 12.6 (s, 1 H), 7.6 (s, 1 H), 7.4 (s, 1 H), 4.0 (m, 12 H), 2.5 (t, 2 H, $J = 7$), 1.9 (m, 12 H), 1.4 (m, 16 H), 0.9 (m, 12 H); MS m/z: 684 (M^+). **AQ-MOH (3):** ν_{max}/cm^{-1}: 2927, 2856, 1710, 1629, 1574, 1427, 1324, 1135; **^{1}H NMR**: δ 12.7 (s, 1 H), 7.6 (s, 1 H), 7.4 (s, 1 H), 4.1 (m, 12 H), 2.4 (t, 2 H, $J = 7.4$), 1.9 (m, 10 H), 1.5 (m, 12 H), 1.3 (m, 34 H), 0.9 (m, 12 H); MS m/z: 895 ($M^+ + 1$). **AQ-MOH (4):** ν_{max}/cm^{-1}: 3296 (w), 2957, 2934, 2872, 1710, 1662, 1629, 1573, 1426, 1321, 1282, 1134; **^{1}H NMR**: δ 12.7 (s, 1 H), 7.6 (s, 1 H), 7.4 (s, 1 H), 4.0 (m, 12 H), 2.37 (t, 2 H, $J = 7.4$), 1.9 (m, 12 H), 1.57 (m, 12 H), 0.9 (m, 12 H); MS m/z: 670 (M^+). **AQ-MOH (5):** ν_{max}/cm^{-1}: 2928, 2857, 1710, 1629, 1574, 1466, 1427, 1324, 1282, 1135; **^{1}H NMR**: δ 12.6 (s, 1 H), 7.6 (s, 1 H), 7.4 (s, 1 H), 4.1 (m, 12 H), 2.3 (t, 2 H, $J = 7.4$), 1.8 (m, 10 H), 1.5 (m, 12 H), 1.3 (m, 26 H), 0.9 (m, 12 H) MS m/z: 839 ($M^+ + 1$). **AQ-MOH (6):** ν_{max}/cm^{-1}: 2925, 2854, 1710, 1629, 1573, 1426, 1324, 1283, 1135; **^{1}H NMR**: δ 12.6 (s, 1 H), 7.6 (s, 1 H), 7.4 (s, 1 H), 4.1 (m, 12 H), 2.3 (t, 2 H, $J = 7.6$), 1.9 (m, 10 H), 1.7 (m, 12 H), 1.29 (m, 42 H), 0.9 (m, 12 H) MS m/z: 951 ($M^+ + 1$). **AQ-MOH (7):** ν_{max}/cm^{-1}: 2927, 2856, 1711, 1629, 1574, 1466, 1426, 1323, 1135; **^{1}H NMR**: δ 12.6 (s, 1 H), 7.6 (s, 1 H), 7.4 (s, 1 H), 4.1 (m, 12 H), 2.4 (t, 2 H, $J = 7.5$), 1.8 (m, 10 H), 1.4 (m, 40 H), 0.9 (m, 12 H); MS m/z: 838 ($M^+ + 1$).

AQ-SR (**3**): ν_{max}/cm^{-1}: 3433 (w), 2924, 2854, 1711, 1660, 1571, 1466, 1324, 1133; **^{1}H NMR**: δ 7.6 (s, 2 H), 4.2 (t, 4 H, $J = 6.5$), 4.1 (q, 8 H, $J = 6.1$), 2.3 (t, 4 H, $J = 7.4$), 1.9 (m, 8 H), 1.8 (m, 4 H), 1.7 (m, 4 H), 1.4 (m, 52 H), 0.9 (m, 12 H); MS m/z: 1036 ($M^+ + 1$).

3.2.2. *General Procedure for the Preparation of Dimers having Hydroxyl Functional Group (**DA-OH**).* A stirred mixture of **AQ-MOH** (0.12 mmol) in dry dichloromethane solution under the nitrogen atmosphere was added to the 1,3-dicyclohexylcarbodiimide (DCC) (0.5 mmol), 4-(*N*,*N*,-dimethylamino)pyridine (DMAP) as a catalyst and finally **TP-OH** (0.14 mmol) was added and the reaction mixture was stirred at RT for 24 h. It was then filtered and solvent was evaporated and the crude product thus obtained was purified by CC on silica gel, by eluting with ethyl acetate: hexane (1:10). Reprecipitation from a mixture of methanol and diethyl ether gave the product **D-A(OH)**, a yellow solid (derivative **1** and **4** only) in 46% yield, and remaining derivatives were semi-solid or gummy at RT and did not reprecipitated in these solvents.

D-A(OH)(1): ^{1}**H NMR**: δ 12.64 (s, 1 H), 8.01 (s, 1 H), 7.86 (unresolved s, 2 H), 7.82 (unresolved s, 2 H), 7.77 (s, 1 H), 7.67 (s, 1 H), 7.37 (s, 1 H), 4.17 (m, 20 H), 3.08 (t, 2 H, $J=7.5$), 2.42 (t, 2 H, $J=6.8$), 1.84 (m, 24 H), 1.54 (m, 12 H), 1.0 (m, 27 H); ^{13}**C NMR**: δ 186.8, 171.7, 158.4, 157.3, 156.4, 154.3, 149.7, 149.5, 149.2, 148.8, 139.9, 130.6, 127.9, 124.6, 123.5, 123.1, 123.0, 121.1, 116.8, 108.0, 107.3, 106.9, 106.5, 106.0, 104.7, 73.9, 73.2, 69.9, 69.5, 69.2, 68.9, 68.5, 32.3, 31.4, 31.0, 30.9, 25.8, 19.3, 19.2, 19.0, 13.9; ν_{max}/cm^{-1}: 3438 (w), 2956, 2872, 1754, 1661, 1620, 1574, 1513, 1433, 1321, 1263, 1135, 1037; UV-vis λ_{max} (ε_{max}): 278 (0.64) nm (10^6 L mol^{-1}cm^{-1}); Anal. calcd. for $C_{72}H_{96}O_{15}$: C, 71.85; H, 8.21. Found: C, 71.66; H, 7.95; MS *m*/*z*: 1200 (M$^+$).

D-A(OH)(2): ^{1}**H NMR**: δ 12.66 (s, 1 H), 8.11 (s, 1 H), 7.85 (unresolved s, 2 H), 7.8 (unresolved s, 2 H), 7.79 (s, 1 H), 7.64 (s, 1 H), 7.36 (s, 1 H), 4.17 (m, 20 H), 2.84 (s, 2 H), 2.13 (s, 4 H), 1.89 (m, 20 H), 1.46 (m, 34 H), 0.93 (m, 27 H); ^{13}**C NMR**: δ 180.5, 158.4, 156.4, 149.4, 148.9, 130.7, 124.6, 123.1, 119.3, 116.7, 108.0, 107.2, 106.9, 106.5, 106.0, 104.7, 74.2, 73.8, 73.5, 69.7, 69.4, 69.2, 68.8, 33.7, 29.9, 29.1, 28.7, 28.3, 28.1, 22.5, 21.6, 14.0; ν_{max}/cm^{-1}: 3439 (w), 2954, 2867, 1754, 1662, 1621, 1574, 1513, 1433, 1321, 1263, 1135; UV-vis λ_{max} (ε_{max}): 278 (1.27) nm (10^6 L mol^{-1}cm^{-1}); MS *m*/*z*: 1340 (M$^+$ + 1).

D-A(OH)(3):^{1}**H NMR**: δ 12.66 (s, 1 H), 8.05 (s, 1 H), 7.85 (unresolved s, 2 H), 7.80 (unresolved s, 2 H), 7.76 (s, 1 H), 7.63 (s, 1 H), 7.37 (s, 1 H), 4.15 (m, 20 H), 2.68 (t, 2 H, $J=7.52$), 1.87 (m, 24 H), 1.52 (m, 94 H), 0.88 (t, 27 H, $J=5.8$); ^{13}**C NMR**: δ 186.8, 180.4, 171.9, 158.3, 157.3, 156.4, 154.6, 149.7, 149.4, 149.2, 148.9, 148.8, 148.0, 139.8, 130.6, 127.8, 124.6, 123.5, 123.1, 121.1, 116.6, 111.3, 108.1, 107.3, 107.0, 106.7, 106.0, 104.7, 74.5, 74.2, 73.5, 69.9, 69.8, 69.5, 69.2, 68.8, 34.1, 31.8, 30.3, 29.4, 29.3, 29.0, 26.1, 21.0, 14.0; ν_{max}/cm^{-1}: 3436 (w), 2925, 2855, 1755, 1662, 1620, 1574, 1513, 1434, 1384, 1322, 1263, 1136, 1040; UV-vis λ_{max} (ε_{max}): 278 (1.21) nm (10^6 L mol^{-1}cm^{-1}); Anal. calcd. for $C_{112}H_{176}O_{15}$: C, 76.23; H, 10.17. Found: C, 76.56; H, 10.05; MS *m*/*z*: 1761 (M$^+$).

D-A(OH)(4): ^{1}**H NMR**: δ 12.65 (s, 1 H), 8.05 (s, 1 H), 7.85 (unresolved s, 2 H), 7.81 (unresolved s, 2 H), 7.77 (s, 1 H), 7.64 (s, 1 H), 7.38 (s, 1 H), 4.16 (m, 20 H), 2.68 (t, 2 H, $J=7.5$), 1.86 (m, 24 H), 1.56 (m, 22 H), 1.01 (m, 27 H); ^{13}**C NMR**: δ 216.9, 209.8, 203.8, 192.7, 186.9, 167.8, 158.3, 157.3, 156.4, 154.7, 149.4, 148.7, 139.9, 130.7, 124.6, 123.8, 123.4, 123.1, 122.4, 121.9, 121.0, 118.7, 116.8, 116.6, 108.0, 107.2, 106.9, 106.7, 105.9, 105.5, 105.1, 104.7, 74.5, 73.8, 73.2, 69.5, 69.4, 69.1, 68.9, 68.4, 34.1, 33.1, 32.7, 32.3, 31.4, 31.0, 30.2, 29.2, 28.3, 25.8, 19.3, 13.9; ν_{max}/cm^{-1}: 3439 (w), 2957, 2871, 1754, 1621, 1575, 1514, 1434, 1321, 1263, 1136, 1037; UV-vis λ_{max} (ε_{max}): 278 (1.5) nm (10^6 L mol^{-1}cm^{-1}); Anal. calcd. for $C_{76}H_{104}O_{15}$: C, 72.47; H, 8.48. Found: C, 72.84; H, 8.24; MS *m*/*z*: 1256 (M$^+$).

D-A(OH)(5): ^{1}**H NMR**: δ 12.66 (s, 1 H), 8.05 (s, 1 H), 7.85 (unresolved s, 2 H), 7.81 (unresolved s, 2 H), 7.77 (s, 1 H), 7.62 (s, 1 H), 7.37 (s, 1 H), 4.16 (m, 20 H), 2.66 (t, 2 H, $J = 7.66$), 1.91 (m, 20 H), 1.42 (m, 66 H), 0.92 (m, 27 H); ν_{max}/cm^{-1}: 3433 (w), 2926, 2858, 1754, 1578, 1513, 1433, 1322, 1263, 1163, 1039; UV-Vis λ_{max} (ε_{max}): 278 (1.15) nm(10^6 L mol^{-1}cm^{-1}); MS m/z: 1564 ($M^+ + 1$).

D-A(OH)(6): ^{1}**H NMR**: δ 12.66 (s, 1 H), 8.05 (s, 1 H), 7.85 (unresolved s, 2 H), 7.81 (unresolved s, 2 H), 7.77 (s, 1 H), 7.62 (s, 1 H), 7.37 (s, 1 H), 4.14 (m, 20 H), 2.66 (t, 2 H, $J = 7.76$), 1.86 (m, 22 H), 1.48 (m, 104 H), 0.88 (m, 27 H); ^{13}**C NMR**: δ 1805, 171.0, 158.0, 157.0, 155.0, 153.0, 149.4, 148.0, 139.8, 130.7, 127.8, 123.1, 121.1, 116.6, 111.3, 108.0, 107.3, 106.9, 106.7, 105.9, 104.7, 74.7, 74.2, 73.6, 69.9, 69.2, 68.8, 34.1, 31.8, 30.3, 29.4, 29.3, 26.1, 26.0, 25.1, 22.6, 14.0; ν_{max}/cm^{-1}: 3434 (w), 2924, 2855, 1754, 1620, 1575, 1514, 1433, 1322, 1263, 1136, 1040; UV-vis λ_{max} (ε_{max}): 278 (1.25) nm (10^6 L mol^{-1}cm^{-1}); Anal. calcd. for $C_{116}H_{184}O_{15}$: C, 76.52; H, 10.30. Found: C, 76.74; H, 10.84; MS m/z: 1817 ($M^+ + 2$).

D-A(OH)(7): ^{1}**H NMR**: δ 12.7 (s, 1 H), 8.05 (s, 1 H), 7.85 (unresolved s, 2 H), 7.80 (unresolved s, 2 H), 7.76 (s, 1 H), 7.63 (s, 1 H), 7.37 (s, 1 H), 4.15 (m, 20 H), 2.68 (t, 2 H, $J = 7.6$), 1.88 (m, 24 H), 1.44 (m, 76 H). 0.90 (t, 27 H, $J = 6.8$); ^{13}**C NMR**: δ 186.9, 171.9, 158.3, 157.3, 156.4, 149.2, 148.0, 139.8, 130.7, 127.9, 123.0, 121.1, 116.6, 111.3, 108.1, 107.3, 107.0, 106.7, 106.0, 104.7, 74.5, 74.2, 73.6, 69.8, 69.5, 69.2, 68.8, 34.1, 31.8, 30.3, 29.1, 26.1, 25.9, 25.1, 22.6, 14.0; ν_{max}/cm^{-1}: 3435 (w), 2926, 2857, 1755, 1661, 1621, 1576, 1434, 1322, 1263, 1136, 1040; UV-vis λ_{max} (ε_{max}): 278 (1.15) nm (10^6 L mol^{-1}cm^{-1}); MS m/z: 1635 ($M^+ + 1$).

D-A(OH)(8): ^{1}**H NMR**: δ 12.7 (s, 1 H), 8.05 (s, 1 H), 7.85 (unresolved s, 2 H), 7.81 (unresolved s, 2 H), 7.77 (s, 1 H), 7.6 (s, 1 H), 7.37 (s, 1 H), 4.16 (m, 20 H), 2.66 (t, 2 H, $J = 7.4$), 1.88 (m, 22 H), 1.56 (m, 24 H), 1.28 (m, 32 H), 1.04 (m, 15 H), 0.86 (t, 12 H, $J = 10.6$); ν_{max}/cm^{-1}: 3436 (w), 2927, 2857, 1751, 1621, 1574, 1513, 1433, 1322, 1262, 1135, 1026; MS m/z: 1480 (M^+).

3.2.3. *General Procedure for the Preparation of* ***D-A(OAc)*** *Dimers (3, 5, 7, and 8).*

The dimer **D-A(OH)** was refluxed in excess of acetic anhydride and pyridine for 18 h under nitrogen atmosphere. The cooled reaction mixture was poured into ice, acidified with 5% HCl, and was extracted with diethylether. The combined extracts were washed with water, saturated NaCl solution, and dried over anhydrous Na_2So_4. The dried crude organic phase was concentrated and purified by CC over silica gel afforded the **D-A(OAc)** type dimer in 85% yield.

D-A(OAc)(3): ^{1}**H NMR**: δ 8.07 (s, 1 H), 7.85 (unresolved s, 2 H), 7.82 (unresolved s, 2 H), 7.78 (s, 1 H), 7.7 (s, 1 H), 7.5 (s, 1 H), 4.16 (m, 14 H), 4.07 (m, 6 H), 2.68 (t, 2 H, $J = 7.0$), 2.48 (s, 3 H), 1.91 (m, 20 H), 1.78 (m, 4 H), 1.49 (m, 94 H), 0.89 (m, 27 H); ^{13}**C NMR**: δ148.9, 139.8, 127.9, 123.1, 116.6, 108.7, 108.1, 107.3, 107.0, 106.6, 106.0, 74.5, 74.1, 69.9, 69.5, 69.1, 68.8, 31.8, 303.3, 29.3, 26.1, 26.0, 25.1, 22.6, 20.9, 14.0; ν_{max}/cm^{-1}: 3438 (w), 2925, 2856, 1760, 1665, 1615, 1575, 1514, 1465, 1435, 1322, 1262, 1128, 1039; UV-vis λ_{max} (ε_{max}) 278 (0.86) nm (10^6 L mol^{-1}cm^{-1}); Anal. calcd. for $C_{105}H_{160}O_{16}$: C, 75.79; H, 10.04. Found: C, 75.39; H, 10.39; MS m/z: 1802 (M^+).

D-A(OAc)(5): ^{1}**H NMR** ($CDCl_3$): δ 8.06 (s, 1 H), 7.85 (unresolved s, 2 H), 7.82 (unresolved s, 2 H), 7.77 (s, 1 H), 7.7 (s, 1 H), 7.54 (s, 1 H), 4.17 (m, 16 H), 4.05 (m, 4 H), 2.66 (t, 2 H, $J = 7.5$), 2.48 (s, 3 H), 1.9 (m, 20 H), 1.75 (m, 4 H), 1.37 (m, 66 H), 0.93

(t, 27 H, $J = 6.8$); **^{13}C NMR** ($CDCl_3$): δ 157.2, 147.4, 123.1, 116.7, 108.7, 108.1, 107.4, 107.0, 106.0, 74.7, 74.0, 69.9, 69.1, 68.8, 34.1, 31.6, 30.2, 29.3, 28.9, 25.8, 25.6, 25.1, 22.6, 20.9, 14.0; ν_{max}/cm^{-1}: 3437 (w), 2928, 2860, 1760, 1663, 1577, 1435, 1382, 1322, 1262, 1128, 1038; UV-vis λ_{max} (ε_{max}): 278.1 (1.16) nm (10^6 L mol^{-1}cm^{-1}); Anal. calcd. for $C_{100}H_{150}O_{16}$: C, 74.59; H, 9.51. Found: C, 74.42; H, 9.28; MS *m/z*: 1606 (M^+).

D-A(OAc)(7): ^{1}H NMR: δ 8.07 (s, 1 H), 7.85 (unresolved s, 2 H), 7.82 (unresolved s, 2 H), 7.78 (s, 1 H), 7.7 (s, 1 H), 4.16 (m, 16 H), 4.07 (m, 4 H), 2.7 (t, 2 H, $J = 7$), 2.48 (s, 3 H), 1.91 (m, 20 H), 1.78 (m, 4 H), 1.49 (m, 76 H), 0.89 (m, 27 H), and 1.1 (m, 15 H); **^{13}C NMR**: δ 108.7, 180.4, 171.9, 169.1, 157.4, 157.2, 154.1, 149.7, 149.4, 149.2, 148.8, 147.3, 145.3, 143.6, 139.8, 132.0, 127.8, 124.6, 123.5, 123.1, 120.3, 118.7, 116.6, 108.7, 108.1, 107.3, 107.0, 106.6, 106.0, 74.5, 74.1, 74.0, 69.8, 69.5, 69.2, 68.8, 34.1, 31.8, 30.3, 29.3, 29.1, 26.1, 25.9, 25.1, 22.6, 20.9, 14.0; ν_{max}/cm^{-1}: 3437 (w), 2927, 2858, 1760, 1730, 1664, 1576, 1513, 1435, 1322, 1263, 1127, 1039; UV-vis λ_{max} (ε_{max}): 278 (1.12) nm (10^6 L mol^{-1}cm^{-1}); Anal. calcd. for $C_{105}H_{160}O_{16}$: C, 75.05; H, 9.74. Found: C, 74.79; H, 10.21; MS *m/z*: 1676 (M^+).

D-A(OAc)(8): ^{1}H NMR: δ 8.06 (s, 1 H), 7.86 (unresolved s, 2 H), 7.81 (unresolved s, 2 H), 7.78 (s, 1 H), 7.7 (s, 1 H), 7.5 (s, 1 H), 4.2 (m, 10 H), 4.16 (m, 4 H), 4.0 (t, 6 H, $J = 6.4$), 2.68 (t, 2 H, $J = 7.6$), 2.48 (s, 3 H), 1.9 (m, 18 H), 1.76 (m, 4 H), 1.58 (m, 24 H), 1.29 (m, 32 H), 1.04 (m, 15 H), 0.88 (m, 12 H); **^{13}C NMR**: δ 181.0, 171.9, 157.4, 149.7, 148.8, 147.3, 145.3, 143.6, 139.8, 132.0, 127.8, 124.6, 123.1, 120.3, 118.7, 116.6, 108.7, 108.0, 107.3, 107.0, 106.7, 105.9, 74.5, 74.0, 69.4, 69.2, 68.4, 32.1, 31.8, 31.4, 30.3, 29.2, 26.0, 25.1, 22.6, 20.9, 19.3, 13.9; ν_{max}/cm^{-1}: 3436 (w), 2927, 2860, 1762, 1577, 1434, 1382, 1321, 1262, 1127, 1037; UV-vis λ_{max} (ε_{max}): 277.9 (1.03) nm (10^6 L mol^{-1}cm^{-1}); Anal. calcd. for $C_{94}H_{138}O_{16}$: C, 73.98; H, 9.25. Found: C, 73.54; H, 9.74; MS *m/z*: 1522 (M^+).

3.2.4. *General Procedure for the Preparation of Trimer **D-A-D(1 and 2)***. A mixture of **TP-OH** (0.16 mmol), K_2CO_3 (1.0 mmol), and α,ω-dibromoalkane (1.3 mmol) in dry methylethylketone (15 ml) was heated at 80°C for 24 h under anhydrous atmosphere. Usual work-up followed by column chromatographic purification afforded the compound **4** in 70% yields. The trimers **D-A-D** were prepared by heating a mixture of **4** (0.12 mmol), K_2CO_3 (0.63 mmol), and **AQ-DOH** (0.12 mmol) in dry DMF at 100°C for 24 h. Standard work-up followed by the purification of the crude product by column chromatography over silica gel yielded the trimers **D-A-D(1 and 2)** in 45% yields.

D-A-D(1): ^{1}H NMR: δ 7.83 (s, 12 H), 7.59 (s, 2 H), 4.22 (m, 24 H), 4.07 (m, 12 H), 1.97 (m, 28 H), 1.78 (m, 8 H), 1.68 (m, 8 H), 1.58 (m, 36 H), 1.33 (m, 58 H), and 0.91 (m, 32 H); **^{13}C NMR**: δ 180.1, 156.4, 152.8, 148.0, 145.9, 131.6, 122.7, 119.4, 106.5, 106.0, 73.5, 73.1, 68.7, 68.1, 30.6, 30.5, 29.3, 28.4, 28.0, 25.1, 24.8, 24.6, 21.6, 13.0; ν_{max}/cm^{-1}: 3434 (w), 2930, 2861, 1665, 1617, 1573, 1514, 1436, 1384, 1321, 1263, 1168, 1043; UV-vis (λ_{max} in nm (ε_{max} in 1 mol^{-1}cm^{-1}), CH_2Cl_2): 345 (0.15×10^6), 310 (0.6×10^6), 278 (2.1×10^6); Anal. calcd. for $C_{146}H_{222}O_{20}$: C, 76.33; H, 9.74. Found: C, 76.08; H, 10.0.

D-A-D(2): ^{1}H NMR ($CDCl_3$): δ 7.83 (s, 12 H), 7.60 (s, 2 H), 4.22 (m, 24 H), 4.15 (t, 4 H, $J = 6.44$), 4.07 (t, 8 H, $J = 6.48$), 1.80 (m, 36 H), 1.54 (m, 44 H) and 1.02 (m, 42 H); **^{13}C NMR** ($CDCl_3$): δ 181.2, 157.4, 153.9, 149.0, 147.0, 132.6, 123.6, 120.4, 108.9, 107.4, 107.0, 74.6, 73.7, 69.7, 69.4, 68.8, 47.9, 32.3, 31.5, 31.1, 30.3, 29.5, 26.2, 26.0, 19.3, 19.2, 13.9; MALDI-TOF-MS[M]$^+$: calcd for $C_{122}H_{172}O_{20}$:1956; found [M^{+1}]$^+$ 1957.3; ν_{max}/cm^{-1}: 3434 (w), 2925, 2869, 1662, 1575, 1514, 1436, 1319, 1262, 1167, 1041; UV-vis (λ_{max} in nm (ε_{max} in 1 mol^{-1} cm^{-1}), CH_2Cl_2): 344 (0.1×10^6), 309 (0.6×10^6), 276 (1.8×10^6); Anal. calcd. for $C_{122}H_{172}O_{20}$: C, 74.73; H, 8.94. Found: C, 75.17; H, 9.13.

3.2.5. *Procedures for the Preparation of Trimer* ***D-A-D(3)***. To a solution of 8,8′-(2,3,6,7-tetrakis(octyloxy)-9,10-dioxo-9,10-dihydroanthracene-1,5-diyl)bis(oxy) dioctanoic acid **(AQ-SR(3))** (104 mg, 0.1 mmol) in CH_2Cl_2 (20 ml) was added to DCC (80 mg, 0.4 mmol) at RT, and stirring was continued for 10 min. Then a suspension of DMAP (35 mg, 0.29 mmol) and **TP-OH** (128 mg, 0.22 mmol) in CH_2Cl_2 was added and the resulting mixture was stirred for 24 h at RT. Then the mixture was filtered via Celite and organic layer was washed with 1 N HCl and water, dried over anhydrous Na_2SO_4, and concentrated. Purification by column chromatography on silica (hexane: CH_2Cl_2) and recrystallized from hexane/ C_2H_5OH was yielded 0.123 g (54%) yellow solid.

^{1}H NMR ($CDCl_3$): δ 8.06 (s, 2 H), 7.86 (s, 4 H), 7.82 (s, 4 H), 7.78 (s, 2 H), 7.76 (s, 2 H), 4.23 (m, 20 H), 4.12 (t, 4 H, $J = 6.44$), 4.07 (m, 8 H), 2.69 (t, 4 H, $J = 7.58$), 1.89 (m, 36 H), 1.59 (m, 46 H), 1.3 (m, 30 H), 1.03 (m, 30 H), 0.87 (m, 8 H); **^{13}C NMR** ($CDCl_3$): δ 181.2, 172.0, 157.5, 153.9, 149.7, 149.5, 149.2, 149.0, 148.8, 147.0, 139.8, 132.7, 127.9, 124.6, 123.5, 123.1, 120.4, 116.7, 108.1, 107.3, 107.0, 106.7, 105.9, 74.6, 74.1, 69.6, 69.2, 69.0, 68.5, 34.1, 31.8, 31.4, 30.3, 29.3, 26.0, 25.9, 25.1, 22.6, 19.3; ν_{max}/cm^{-1}: 3435 (w), 2930, 2866, 1753, 1663, 1616, 1572, 1514, 1435, 1319, 1263, 1136, 1040; UV-vis (λ_{max} in nm (ε_{max} in L mol^{-1}cm^{-1}), CH_2Cl_2): 344 (0.1×10^6), 306 (0.6×10^6), 276 (1.9×10^6); Anal. calcd. for $C_{138}H_{200}O_{22}$: C, 74.96; H, 9.12. Found: C, 75.33; H, 9.59; MALDI-TOF-MS [M]$^+$: 2210 [M$^+$ + 2].

4. Conclusion

A variety of dimers and trimers bearing triphenylene and anthraquinone have been prepared. Many of them exhibit the N and Col mesophases at room temperature, some of them even form glassy state. The variation of the mesomorphic behavior of these compounds appeared to be dependent on the relationship of the lengths between the spacer and peripheral alkoxy chains. Among two substituents to anthraquinone, i.e., hydroxyl and acetyloxy groups, the latter destabilizes mesomorphic behavior. Three trimers studied exhibit no, Col, and N mesophases depending on the relationship of the length of spacer and the peripheral chain lengths of donor and acceptor. The ester linking functional group destroy the ordered molecular self-assembly of columnar mesophase to disordered nematic mesophase. Thus molecular architecture and associated functional groups can change the molecular self-assembly and transition temperatures.

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