Journal of Materials Chemistry

ELECTRONIC SUPPLEMENTARY INFORMATION

Synthesis, optical and structural properties of sanidic liquid crystal (cholesteryl)benzoate-ethynylene oligomers and polymer

Griselda Castruita[a], Vladimir García[a,b,] Eduardo Arias*[a] , Ivana Moggio[a], Ronald Ziolo[a], Arturo Ponce[a], Virgilio González[b], Joy E. Haley[c], Jonathan L. Flikkema[d] and Thomas Cooper[c]

[a]Centro de Investigación en Química Aplicada (CIQA), Boulevard Enrique Reyna 140, 25253 Saltillo, México. Tel: +52 844 438 98 30. Fax: +52 844 438 98 39. E-mail: earias@ciqa.mx.

[b] Facultad de Ing. Mecánica y Eléctrica, Universidad Autónoma de Nuevo León, Pedro de Alba, Cd. Univ. 66450 San Nicolás de los Garza, México.

[c] Materials and Manufacturing Directorate, Air Force Research, Laboratory, Wright-Patterson Air Force Base, OH 45433, USA.

[d] SOCHE Student Research Program Dayton, OH 45420, USA.

Content

I. Experimental procedures and characterization of all compounds.

Materials. The following chemical reagents: 2-amino-5-yodo benzoic acid, bis(triphenyl phosphine) palladium (II) dichloride, cholesterol, cuprous iodide, 2,5-dibromo benzoic acid, *N,N'*-dicyclohexylcarbodiimide (DCC), 4-(dimetylamino) pyridine (DMAP), dimethylamine, iodomethane, tetrabutylamonium fluoride (TBAF, 1M in THF), trimethylsilylacetylene (TMSA), boron trifluoride diethyl etherate (BF_3•OEt_2) and *tert*-butyl nitrite were obtained from Aldrich and used as received. $CHCl_3$, CH_2Cl_2 and hexanes were purchased from J.T. Backer. Triethylamine (Et_3N) (Aldrich) was distilled from KOH, THF (Aldrich) was also first distilled from KOH and then from sodium benzofenone until the typical blue complex was formed. All solvents used for optical characterization were spectroscopic grade from Aldrich.

Synthesis of 2-(diazonium tetrafluoroborate)-5-iodobenzoic acid (2). A round-bottom flask was charged with BF_3•OEt_2 (86.45 mmol, 10.95 mL) and cooled to -15 ºC. Then, **1** (38 mmol, 10 g) in dry THF (150 mL) was added drop wise with an addition funnel under argon. After formation of a homogenous paste, *tert*-butyl nitrite (86.45 mmol, 10.31 mL) in dry THF (150 mL) was added drop wise keeping always the internal temperature at –15ºC. The mixture was warmed to 5 - 7ºC and then, cold hexane was added. The resulting diazonium tetrafluoroborate salt was filtered off by suction and washed with cold diethyl ether (4x100 mL). The pale pink powder was air-dried and obtained in 97 % yielding**.** mp 168-170ºC; ^1H NMR (200 MHz, DMSO-d_6): δ(ppm) 8.57(s, 1H, -PhH), 8.54(d, 1H, -PhH), 8.40(s, 1H, -PhH), 8.40(s, 1H, -COOH); Anal. Calcd (%) for $C_7H_4BF_4IN_2O_2$: C, 23.24; H, 1.11; N, 7.74. Found: C, 23.20; H, 1.28; N, 7.85.

Synthesis of 2-(3,3-diethyltriazene)-5-iodobenzoic acid (3). Diethylamine (75.8 mmol, 7.84 mL) and K_2CO_3 (58.33 mmol, 8.06 g) in DMF (200 mL) were taken up in a round bottomed flask and cooled to –10ºC with vigorous stirring. Then, a diazonium tetrafluoroborate salt **(2)** (29.16 mmol, 10 g) in DMF (80 mL) was added portion-wise and stirred until the temperature reached the 10ºC. Later, water (400 mL) was added and the mixture was acidified (HCl) to obtain a pH of 3. The organic layer was extracted with CH_2Cl_2 (3X100 mL) and the solvents were vacuum removed. The crude product was passed through a short column of silica gel ($CHCl_3$/MeOH, 50/1, Rf=0.7) to obtain yellow crystals in 66 % yielding**.** mp 95-98 ºC; ^1H NMR (200 MHz, $CDCl_3$): δ(ppm) 13.80(s, 1H, -COOH), 8.47(s, 1H, -PhH), 7.69(dd, 1H, -PhH), 7.39(d, 1H, -PhH), 3.90(qu, 2H,-NCH_2-), 1.40(t, 3H, -NCH_3), 1.26(t, 3H, -NCH_3). NMR ^{13}C ($CDCl_3$, 75 MHz) δ (ppm): 10.2 (C-β-N), 14.2 (C-β-N), 43.6 (C-α-N), 51.3 (C-α-N), 89.6 (C5), 117.8 (C3), 123.0 (C1), 140.8 (C6), 142.2 (C4), 148.4 (C2), 166.4 (O=C-OH). Anal. Calcd (%) for $C_{11}H_{14}IN_3O_2$: C, 38.06; H, 4.06; N, 12.10; O, 9.22. Found: C, 38.18; H, 4.13; N, 11.91; O, 9.27.

Synthesis of 2-[(3,3-diethyltriazene)]-5-[iodo] (cholesteryl) benzoate (4). 3 (3g, 8.64mmol), cholesterol (3.3414g, 8.64mmol), DMAP (100mg, 0.82mmol) and 70mL of CH_2Cl_2 were charged in a two necked flask topped with a calcium oxide guard tube and cooled at 0°C. Then a solution of DCC (1.7831g, 8.64mmol in 10 mL of CH_2Cl_2) was drop wise added. The reaction was left to reach the room temperature and stirred for 15h. The precipitated urea was filtered off and the filtrate was evaporated under vacuum. The crude product was purified by chromatography (SiO_2, $CHCl_3$, Rf=0.9) to obtain a brown powder in 67% yielding. m.p.102-106°C. ^1H NMR (300MHz, $CDCl_3$): δ (ppm) 7.85 (s, 1H, -PhH), 7.65 (d, 1H, -PhH), 7.19 (d, 1H, -PhH), 5.40 (d, 1H, -C=CH-), 4.82 (m, 1H, -COOCH-), 3.77 (c, 4H, -NCH_2-), 2.44 (d, 2H, -CH_2-β-COO), 2.1-0.85 (m, 44H, -CH_3, -CH_2, -CH, CH_3-β-N), 0.67 (s, 3H, -CH_3). NMR

^{13}C ($CDCl_3$, 75 MHz) δ (ppm): 0.95, 18.8, 19.4, 21.15, 22.65, 22.9, 23.9, 24.4, 27.8, 28.1, 28.3, 31.95, 32.0, 35.9, 36.3, 36.7, 37.1, 38.1, 39.6, 39.8, 42.4, 50.1, 56.3, 56.8 (C_{chol}), 11.0 (C-β-N), 14.1 (C-β-N), 41.0 (C-α-N), 49.8 (C-α-N), 77.3 (C-α-O-C=O), 87.8 (C5), 121.0 (C1), 122.8 (CH=C_{chol}), 129.3 (C6), 137.5 (C4), 139.9 (CH=C_{chol}), 149.4 (C2), 166.7 (O=C-O). UV-Vis ($CHCl_3$); λmax (327 nm), ε(8.99 X 10^3 $M^{-1}cm^{-1}$). FT-IR (KBr pellet, cm^{-1}); 3362, 3303, 2927, 2850, 1725, 1647, 1632, 1465, 1415, 1384, 1349, 1342, 1331, 1290, 1265, 1246, 1232, 1197, 1137, 1112, 1076, 1029.ito

Synthesis of 2-[(3,3-diethyltriazene)]-5-[(trimethylsilyl)ethynyl] (cholesteryl) benzoate (5). Bis(triphenylphosphine) palladium (II) dichloride (105.9mg, 0.151mmol), cuprous iodide (28.7mg, 0.151mmol) and **4** (3.599g, 5.028mmol) were charged under nitrogen in a two-necked flask. Then, dry and degassed triethylamine (70mL) was added and stirred until all products were dissolved. Later, trimethylsilylacetylene (1.1mL, 7.54mmol) was added and the reaction mixture was stirred and heated at 60°C under nitrogen overnight. After cooling, the ammonium salt was filtered off and washed with THF. Then the solvents were removed under vacuum. The crude product was purified by chromatography (SiO_2, CH_2Cl_2, Rf=0.7) to obtain a brown powder in 95% yielding. m.p. 112-114°C. ^1H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.67 (s, 1H, -PhH), 7.45 (d, 1H, -PhH), 7.38 (d, 1H, -PhH), 5.40 (d, 1H, -C=CH-), 4.82 (m, 1H, -COOCH-), 3.77 (c, 4H, -NCH_2-), 2.44 (d, 2H, -CH_2-β-COO), 2.1-0.85 (m, 44H, -CH_3, -CH_2, -CH, CH_3-β-N), 0.67 (s, 3H, -CH_3), 0.25 (s, 9H, -$SiCH_3$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 0.1 (Si-CH_3) 11.95, 18.8, 19.4, 21.15, 22.65, 22.9, 23.9, 24.4, 27.8, 28.1, 28.3, 31.95, 32.0, 35.9, 36.3, 36.7, 37.1, 38.1, 39.6, 39.8, 42.4, 50.1, 56.3, 56.8 (C_{chol}), 11.5 (C-β-N), 14.5 (C-β-N), 41.6 (C-α-N), 49.2 (C-α-N), 74.7 (C-α-O-C=O), 94.4 (Si-C≡C), 104.8 (Si-C≡C), 118.8 (C3), 119.1 (C5), 122.7 (CH=C_{chol}), 127.5 (C1), 132.9 (C6), 134.4 (C4), 139.8 (CH=C_{chol}), 149.4 (C2), 167.5 (O=C-O). UV-Vis ($CHCl_3$); λmax(341 nm), ε(2.80 X 10^4 $M^{-1}cm^{-1}$). FT-IR (KBr pellet, cm^{-1}); 3379, 2950, 2868, 2155, 1727, 1597, 1561, 1466, 1453, 1416, 1392, 1350, 1341, 1328, 1298, 1249, 1232, 1202, 1135, 1110, 1076, 1028.

Synthesis of 2-[(3,3-diethyltriazene]-5-[ethynyl] (cholesteryl) benzoate (6). A round-bottom flask charged with **5** (3.7g, 5.39mmol) was dissolved in 50mL of THF. Then, a 1M solution of tetrabutylammonium fluoride (2mL, 6.91mmol) and two drops of distilled water were added. After being stirred for 1h at room temperature, the reaction was stopped by passing through a plug of silica gel. The THF was evaporated and the product was dried in vacuum to give a dark brown viscous liquid in 99% yielding. ^1H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.70 (s, 1H, -PhH), 7.48 (d, 1H, -PhH), 7.40 (d, 1H, -PhH), 5.40 (d, 1H, -C=CH-), 4.82 (m, 1H, -COOCH-), 3.77 (c, 4H, -NCH_2-), 3.1 (s, 1H, -C≡CH), 2.44 (d, 2H, -CH_2-β-COO), 2.1-0.85 (m, 44H, -CH_3, -CH_2, -CH, CH_3-β-N), 0.67 (s, 3H, -CH_3). NMR ^{13}C ($CDCl_3$, 75 MHz) δ (ppm): 11.95, 18.8, 19.4, 21.15, 22.65, 22.9, 23.9, 24.4, 27.8, 28.1, 28.3, 31.95, 32.0, 35.9, 36.3, 36.7, 37.1, 38.1, 39.6, 39.8, 42.4, 50.1, 56.3, 56.8 (C_{chol}), 11.4 (C-β-N), 14.5 (C-β-N), 41.7 (C-α-N), 49.2 (C-α-N), 74.8 (C-α-O-C=O), 77.5 (C≡CH), 83.3(C≡CH), 118.0 (C5), 119.0 (C3), 122.7 (CH=C_{chol}), 127.5 (C1), 133.0 (C6), 134.5 (C4), 139.8 (CH=C_{chol}), 149.8 (C2), 167.3 (O=C-O).

Synthesis of (cholesteryl) 2,5-dibromobenzoate (8). This compound was synthesized applying the same procedure to prepare **4**. In a two necked flask topped with a calcium oxide guard **7** (8g, 28.6mmol), cholesterol (12.1643g, 28.6mmol), DMAP (150mg, 0.23mmol) and DCC (5.9g, 28.6mmol) were introduced and stirred for 15 h. The crude product was purified by chromatography (SiO_2, CH_2Cl_2, Rf=0.9) to give a white powder in 85% yielding. m.p.147-153°C. ^1H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.85 (s, 1H, -PhH), 7.49 (d, 1H, -PhH), 7.41 (d, 1H, -PhH), 5.40 (d, 1H, -C=CH-), 4.85 (m, 1H, -COOCH-), 2.48 (d, 2H, -CH_2-β-COO), 2.1-0.85 (m, 38H, -CH_3, -CH_2, -CH), 0.67 (s, 3H, -CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 11.95, 18.8, 19.4, 21.15, 22.65, 22.9, 23.9, 24.4, 27.8, 28.1, 28.3, 31.95, 32.0, 35.9, 36.3, 36.7, 37.1, 38.1, 39.6, 39.8, 42.4, 50.1, 56.3, 56.8 (C_{chol}), 77.3 (C-α-O-C=O), 120.3 (C5), 121.1 (C2), 123.2 (CH=C_{chol}), 134.0 (C6), 134.6 (C1), 135.2 (C3), 135.6 (C4), 139.4 (CH=C_{chol}), 164.4 (O=C-O). UV-Vis ($CHCl_3$); λmax(294 nm), ε(1.5 X 10^3 $M^{-1}cm^{-1}$).

Synthesis of 2,5-di[(trimethylsilyl) ethynyl] (cholesteryl) benzoate (9). This compound was synthesized applying the same procedure to prepare **5**. **8** (2g, 3.08mmol), (64.93mg, 0.093mmol) of bis(triphenylphosphine) palladium (II) dichloride, cuprous iodide (17.62mg, 0.093mmol) and TMSA (1.1mL, 7.71mmol) were introduced in a two necked flask and reacted overnight. The crude product was purified by chromatography (SiO_2, hexanes/$CHCl_3$ 2/1, Rf=0.6) to give a yellow powder in 75% yielding. m.p. 77-81°C. ^1H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.93 (s, 1H, -PhH), 7.48 (m, 2H, -PhH), 5.40 (d, 1H, -C=CH-), 4.90 (m, 1H, -COOCH-), 2.48 (d, 2H, -CH_2-β-COO), 2.1-0.85 (m, 38H, -CH_3, -CH_2, -CH), 0.68 (s, 3H, -CH_3), 0.24 (s, 18H, -$SiCH_3$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 0 (Si-CH_3), 11.95, 18.8, 19.4, 21.15, 22.65, 22.9, 23.9, 24.4, 27.8, 28.1, 28.3, 31.95, 32.0, 35.9, 36.3, 36.7, 37.1, 38.1, 39.6, 39.8, 42.4, 50.1, 56.3, 56.8 (C_{chol}), 75.5 (C-α-O-C=O), 97.4 (Si-C≡C), 101.7 (Si-C≡C), 103.1 (Si-C≡C), 103.6 (Si-C≡C), 122.9 (CH=C_{chol}), 123.0 (C5), 123.2 (C2), 133.1 (C1), 133.6 (C6), 134.2 (C3), 134.8 (C4), 139.7 (CH=C_{chol}), 165.2 (O=C-O). UV-Vis ($CHCl_3$); λmax(291, 313, 325 nm), ε(2.98 X 10^4, 7.93 X 10^3, 5.93 X 10^3 $M^{-1}cm^{-1}$). FT-IR (KBr pellet, cm^{-1}); 3384, 2951, 2868, 2160, 1731, 1713, 1609, 1480, 1466,1407, 1383, 1320, 1293, 1248, 1206, 1140, 1074, 1029.

Synthesis of (cholesteryl) 2,5-diethynyl benzoate (10). This compound was synthesized applying the same procedure to prepare **6. 9 (**0.45g, 0.657mmol) and tetrabutylammonium fluoride (0.5mL, 1.73mmol) were reacted to give pale orange powder in 98% yielding. m.p. 119-122°C. ^1H NMR (300 MHz, $CDCl_3$): δ(ppm) 8.03 (s, 1H –PhH), 7.55 (d, 2H, -PhH), 5.40 (d, 1H, -C=CH-), 4.87 (m, 1H, -COOCH-), 3.47 (s, 1H, -C≡CH-), 3.20 (s, 1H, -C≡CH-), 2.48 (d, 2H, -CH_2-β-COO), 2.1-0.85 (m, 38H, -CH_3, -CH_2, -CH), 0.67 (s, 3H, -CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 11.95, 18.8, 19.4, 21.15, 22.65, 22.9, 23.9, 24.4, 27.8, 28.1, 28.3, 31.95, 32.0, 35.9, 36.3, 36.7, 37.1, 38.1, 39.6, 39.8, 42.4, 50.1, 56.3, 56.8 (C_{chol}), 75.4 (C-α-O-C=O), 80.0 (C≡CH), 81.7 (C≡CH), 82.2 (C≡CH), 84.2 (C≡CH), 122.5 (C2), 122.9 (C5), 123.0 (CH=C_{chol}), 133.3 (C1), 133.9 (C6), 134.7 (C3), 135.0 (C4), 139.6 (CH=C_{chol}), 164.7 (O=C-O). UV-Vis ($CHCl_3$); λmax(276, 306, 316 nm), ε(3.26 X 10^4, 4.27 X 10^3, 3.57 X 10^3 $M^{-1}cm^{-1}$). FT-IR (KBr pellet, cm^{-1}); 3360, 3249, 2927, 2850, 2103, 1714, 1659, 1631, 1467, 1439, 1412, 1383, 1369, 1316, 1295, 1252, 1194, 1140, 1079, 1028, 1014.

Synthesis of triazene-terminated trimer (11). This compound was synthesized applying the same procedure to prepare **5. 8 (**1.74g, 2.69mmol**)**, **6** (3.3g, 5.38mmol**)**, bis(triphenylphosphine) palladium (II) dichloride (56.6mg, 0.081mmol) and cuprous iodide (15.4mg, 0.081mmol) in 150 mL of Et_3N/THF (80/20 v/v) were reacted over night at 50°C under nitrogen. The crude product was purified by chromatography (SiO_2, $CHCl_3$, Rf=0.6) to give a deep brown powder in 74% yielding. m.p. 121-130°C. ^1H NMR (300 MHz, $CDCl_3$): δ(ppm) 8.1 (s, 1H, -PhH), 7.76 (s, 1H, -PhH), 7.75 (s, 1H, -PhH), 7.6-7.4 (m, 6H, -PhH), 5.40 (s, 3H, -C=CH-), 4.85 (m, 3H, -COOCH-), 3.75 (c, 8H, -NCH_2-), 2.45 (m, 6H, -CH_2-β-COO), 2.1-0.85 (m, 126H, -CH_3, -CH_2, -CH, CH_3-β-N), 0.67 (s, 9H, -CH_3). ^{13}C NMR (75MHz, $CDCl_3$): δ(ppm) 11.95, 18.8, 19.4, 21.15, 22.65, 22.9, 23.9, 24.4, 27.8, 28.1, 28.3, 31.95, 32.0, 35.9, 36.3, 36.7, 37.1, 38.1, 39.6, 39.8, 42.4, 50.1, 56.3, 56.8 (C_{chol}), 75.4 (C-α-O-C=O), 11.0 (C-β-N), 14.1 (C-β-N), 41.0 (C-α-N), 49.8 (C-α-N), 75.9 (C-α-O-C=O), 88.9 (C≡C), 118.6 (C4, C13), 119.10 (C2, C15), 122.75 (C7), 122.9 (C6, C17), 123.15 (CH=C_{chol}), 127.7 (C10), 132.7 (C11), 133.5 (C8), 133.9 (C5, C18), 134.1 (C9), 134.2 (C3, C14), 139.7 (C12), 139.85 (CH=C_{chol}), 149.6 (C1, C16), 165.2 (O=C-O), 167.2 (O=C-O). UV-Vis ($CHCl_3$); λmax(377 nm), ε(7.04 X 10^4 $M^{-1}cm^{-1}$).

Synthesis of iodine-terminated trimer (12).A heavy-walled glass flask equipped with a teflon screw valve was charged with **11** (1.21g, 0.708 mmol) and distilled iodomethane (10mL). The solution was placed under vacuum and the flask was sealed and heated under vigorous stirring at 110°C overnight. After cooling, the remained iodomethane was vacuum removed. Then, THF was added and the precipitate was filtered off. After THF evaporation, the crude product was purified by chromatography (SiO_2, hexane/$CHCl_{3,}$3/1, Rf=0.8) and then by preparative GPC chromatography (Biorads, Bio-Beds SX1, chloroform) to afford a pale yellow powder in 86% yielding. m.p. 217-221°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 8.12 (s, 1H, -PhH), 8.00-7.87 (m, 4H, -PhH), 7.63 (s, 2H, -PhH), 7.30 (d, 2H, -PhH), 5.42 (m, 3H, -C=CH-), 4.90 (m, 3H, -COOCH-), 2.48 (m, 6H, -CH_2-β-COO), 2.1-0.85 (m, 114H, -CH_3, -CH_2, -CH), 0.67 (s, 9H, -CH_3). ^{13}C NMR (75MHz, $CDCl_3$): δ(ppm) 11.95, 18.8, 19.4, 21.15, 22.65, 22.9, 23.9, 24.4, 27.8, 28.1, 28.3, 31.95, 32.0, 35.9, 36.3, 36.7, 37.1, 38.1, 39.6, 39.8, 42.4, 50.1, 56.3, 56.8 (C_{chol}), 75.5 (C-α-O-C=O), 76.1 (C-α-O-C=O), 90.3 (C1, C16), 94.4 (C≡C), 121.6 (C7), 123.0 (C4, C13), 123.1 (CH=C_{chol}), 123.4 (C10), 133.7 (C11), 134.2 (C8), 134.5 (C9), 135.3 (C5, C18), 136.1 (C2, C15), 139.4 (C12), 139.5 (C3, C14), 141.4 (CH=C_{chol}), 141.6 (C6, C17), 165.1 (O=C-O), 165.4 (O=C-O). Anal. Calcd (%) for $C_{106}H_{144}I_2O_2$: C, 72.01; H, 8.21. Found: C, 71.62; H, 8.62. UV($CHCl_3$): λ_{max}(344 nm), ε(7.970 X 10^3 L mol^{-1} cm^{-1}**.** Fluorescence ($CHCl_3$): λ_{max}= 370 nm. Raman ν_{Max} (powder, laser 830nm)/cm^{-1} 2202 (-C≡C-).

Synthesis of triazene-terminated pentamer (13). This compound was synthesized applying the same procedure to prepare **5. 12** (1.98g, 1.12mmol)**, 6** (1.37g, 2.24mmol), bis(triphenylphosphine) palladium (II) dichloride (23.58mg, 0.034 mmol) and cuprous iodide (6.40mg, 0.034mmol) in 100 mL of Et_3N/THF (80/20 v/v). The crude product was purified by chromatography (SiO_2, $CHCl_3$, Rf=0.6) to give a deep brown powder in 75% yielding. m.p. 221-224°C). ^{1}H NMR (300 MHz, CDCl3): δ(ppm) 8.15 (m, 3H, -PhH), 7.75 (s, 2H, -PhH), 7.65-7.40 (m, 10H, -PhH), 5.40 (s, 5H, -C=CH-), 4.90 (m, 5H, -COOCH-), 3.78 (m, 8H, -NCH_2-), 2.45 (m, 10H, -CH_2-β-COO), 2.1-0.85 (m, 202H, -CH_3, -CH_2, -CH, CH_3-β-N), 0.65 (s, 15H, -CH_3). ^{13}C NMR (75MHz, $CDCl_3$): δ(ppm) 11.95, 18.8, 19.4, 21.15, 22.65, 22.9, 23.9, 24.4, 27.8, 28.1, 28.3, 31.95, 32.0, 35.9, 36.3, 36.7, 37.1, 38.1, 39.6, 39.8, 42.4, 50.1, 56.3, 56.8 (C_{chol}), 11.0 (C-β-N), 14.1 (C-β-N), 41.0 (C-α-N), 49.8 (C-α-N), 74.8 (C-α-O-C=O), 75.4 (C-α-O-C=O), 88.8 (C≡C), 119.0 (C4, C25), 122.7 (C2, C27), 122.9 (C6, C10, C16, C19, C29), 123.0 (CH=C_{chol}), 127.3 (C7, C13, C22), 132.75 (C12, C14, C23), 132.9 (C9, C17, C20), 133.8 (C5, C30), 134.1 (C8, C18, C21), 134.2 (C11, C15, C24), 139.6 (C3, C26), 139.9 (CH=C_{chol}), 149.7 (C1, C28), 165.1 (O=C-O), 167.3 (O=C-O). UV-Vis ($CHCl_3$); λmax(379 nm), ε(1.78 X 10^5 $M^{-1}cm^{-1}$).

Synthesis of iodine-terminated pentamer (14). This compound was synthesized applying the same procedure to prepare **12. 13** (1.25g, 0.455mmol) and 10 mL of iodomethane were placed under vacuum and the flask was sealed and heated under vigorous stirring at 110°C overnight. The crude product was purified by precipitation in methanol, by chromatography (SiO_2, $CHCl_3$/hexane 3/1, Rf=0.8) and by preparative GPC chromatography (Biorads, Bio-

Beds SX1, chloroform) to afford yellow powder in 48% yielding. m.p. 276-284°C. ^{1}H NMR (300 MHz, CDCl3): δ(ppm) 8.15 (m, 3H, -PhH), 7.95 (m, 4H, -PhH), 7.65 (m, 6H, -PhH), 7.30 (d, 2H, -PhH), 5.40 (m, 5H, -C=CH-), 4.90 (m, 5H, -COOCH-), 2.50 (d, 10H, -CH$_2$-β-COO), 2.1-0.85 (m, 190H, -CH$_3$, -CH$_2$, -CH), 0.65 (s, 15H, -CH$_3$). ^{13}C NMR (75MHz, CDCl$_3$): δ(ppm) 11.95, 18.8, 19.4, 21.15, 22.65, 22.9, 23.9, 24.4, 27.8, 28.1, 28.3, 31.95, 32.0, 35.9, 36.3, 36.7, 37.1, 38.1, 39.6, 39.8, 42.4, 50.1, 56.3, 56.8 (C$_{chol}$), 75.5 (C-α-O-C=O), 76.1 (C-α-O-C=O), 91.1 (C1, C28), 94.4 (C≡C), 122.96 (C4, C25), 123.12 (CH=C$_{chol}$), 123.38 (C10, C16, C19), 123.44 (C7, C13, C22), 133.0 (C12, C14, C23), 133.8 (C9, C17, C20), 134.2 (C8, C18, C21), 134.8 (C5, C30), 136.1 (C11, C15, C24), 136.8 (C2, C27), 139.4 (CH=C$_{chol}$), 139.5 (C3, C26), 141.5 (C6, C29), 164.8 (O=C-O), 165.2 (O=C-O). Anal. Calcd (%) for $C_{178}H_{240}I_2O_{10}$: C, 76.53; H, 8.86. Found: C, 76.32; H, 8.668. UV(CHCl$_3$): λ$_{max}$(364 nm), ε(1.425 X 10^{5} L mol^{-1} cm^{-1}. Fluorescence (CHCl$_3$): λ$_{max}$= 405 nm. Raman ν$_{Max}$ (powder, laser 830nm)/cm^{-1} 2200 (-C≡C-).

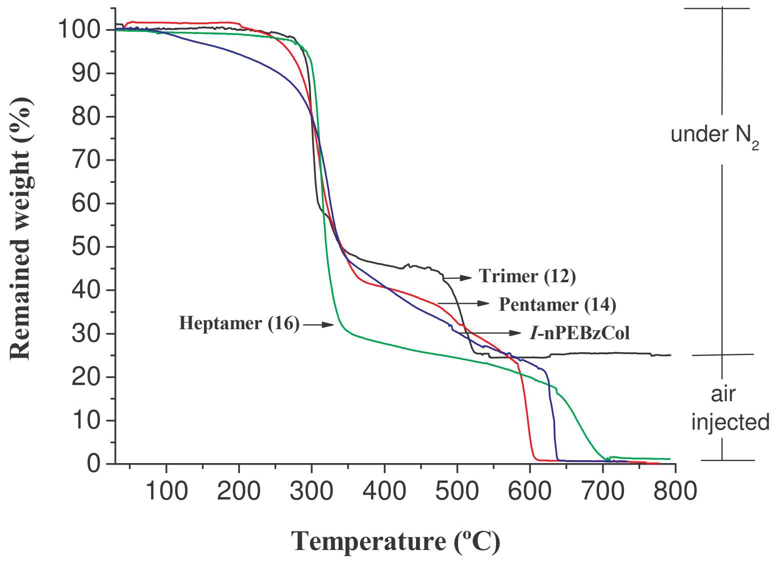
Synthesis of hydrogen-terminated heptamer (15). This compound was synthesized applying the same procedure to prepare **5. 14** (145.5 mg 0.052 mmol)**,** (cholesteryl) 3-ethynylbenzoate (107.2mg, 0.28mmol), bis(triphenylphosphine) palladium (II) dichloride (5mg, 0.015 mmol) and cuprous iodide (spatula) in 17 mL of Et$_3$N and 3 mL of THF were stirred for 48 h at room temperature and then heated at 60°C overnight. After filtered off the ammonium salts and the solvents vacuum evaporated, the crude product was purified by precipitation in methanol and then by chromatography (SiO$_2$, hexane/CHCl$_{3,}$3/1, Rf=0.8) and finally by preparative GPC chromatography (Biorads, Bio-Beds SX1, chloroform) to afford a deep orange powder in 48 % yielding. ^{1}H NMR (300 MHz, CDCl$_3$): δ(ppm) 8.23 (m, 2H, Ar-H-3, H-38), 8.15 (m, 5H, Ar-H-11, H-15, H-23, H-26, H-30), 8.01 (m, 2H, Ar-H-1, H-40), 7.73 (m, 2H, Ar-H-5, H-42), 7.64 (m, 10H, Ar-H-8, H-9, H-17, H-18, H-20, H-21, H-29, H-30, H-32, H-33), 7.44 (m, 2H, Ar-H-6, H-41), 5.40 (s, 7H, 7 x CH=C), 4.89 (m, 7H, 7 x CH-α-O-C=O), 2.48 (m, 14H, 7 x CH$_2$-β-O-C=O), 0.85-2.1 (m, 266 H, 28 x CH$_3$, 70 x CH$_2$, 42 x CH), 0.67 (s, 21H, 7 x CH$_3$-C). UV(CHCl$_3$): λ$_{max}$(374 nm), ε(6.255 X 10^{5} L mol^{-1} cm^{-1}). Fluorescence (CHCl$_3$): λ$_{max}$= 4135 nm.

Synthesis of triazene-terminated heptamer (16). This compound was synthesized applying the same procedure to prepare **5. 14** (0.55g, 0.197mmol)**, 6** (0.27g, 0.433mmol), bis(triphenylphosphine) palladium (II) dichloride (4.14mg, 0.0059mmol) and cuprous iodide (1.12mg, 0.0059mmol) in 150 ml of Et$_3$N/THF (80/20 v/v) were reacted over night at 50°C under nitrogen. The crude product was purified by chromatography (SiO$_2$, CHCl$_3$, Rf=0.6) to afford brown solid in 58% yieldig. m.p. 230-235°C. ^{1}H NMR (300 MHz, CDCl3): δ(ppm) 8.15 (m, 3H, -PhH), 7.75-7.40 (m, 18H, -PhH), 5.40 (s, 7H, -C=CH-), 4.90 (m, 7H, -COOCH-), 3.78 (m, 8H, -NCH$_2$-), 2.45 (m, 14H, -CH$_2$-β-COO), 2.1-0.85 (m, 278H, -CH$_3$, -CH$_2$, -CH, CH$_3$-β-N), 0.65 (s, 21H, -CH$_3$). ^{13}C NMR (75MHz, CDCl$_3$): δ(ppm) 11.95, 18.8, 19.4, 21.15, 22.65, 22.9, 23.9, 24.4, 27.8, 28.1, 28.3, 31.95, 32.0, 35.9, 36.3, 36.7, 37.1, 38.1, 39.6, 39.8, 42.4, 50.1, 56.3, 56.8 (C$_{chol}$), 11.0 (C-β-N), 14.1 (C-β-N), 41.0 (C-α-N), 49.8 (C-α-N), 74.5 (C-α-O-C=O), 74.8 (C-α-O-C=O), 81.7 (C≡C), 117.5 (C4, C37), 119.0 (C6, C41), 122.8 (C2, C10, C16, C22, C25, C31, C39), 123.0 (CH=C$_{chol}$), 127.7 (C7, C13, C19, C28, C34), 133.6 (C8, C18, C20, C29, C33), 133.7 (C11, C15, C23, C26, C36), 134.2 (C3, C38), 134.9 (C12, C14, C24, C27, C35), 139.4 (C9, C17, C21, C30, C32), 139.5 (C5, C42), 139.8 (CH=C$_{colesterilo}$), 150.10 (C1, C40), 165.2 (O=C-O), 167.15 (O=C-O).

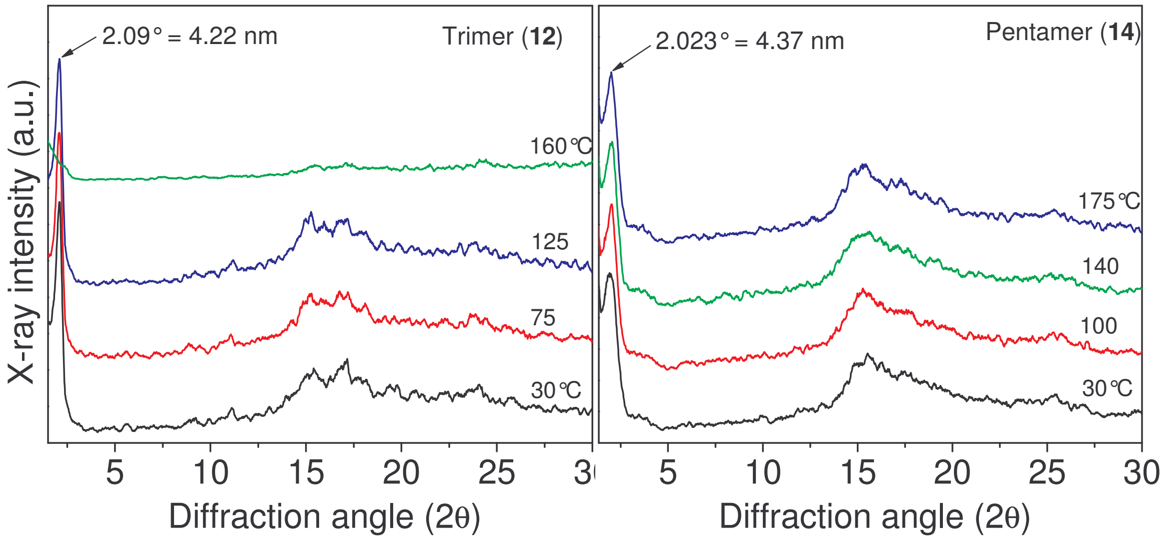
Synthesis of iodine-terminated heptamer (17). This compound was synthesized applying the same procedure to prepare **12. 16** (0.33g, 0.088mmol) and 7 mL of iodomethane were placed under vacuum and the flask was sealed and heated under vigorous stirring at 110°C overnight.The crude product was purified by chromatography (SiO_2, $CHCl_3$/hexane 3/1, Rf=0.9) and then by preparative GPC chromatography (Biorads, Bio-Beds SX1, chloroform) to afford a pale yellow powder in 41% yield. m.p. 257-263°C. ^{1}H NMR (300 MHz, CDCl3): δ(ppm) 8.15 (m, 5H, -PhH), 7.95 (m, 4H, -PhH), 7.65 (m, 10H, -PhH), 7.30 (d, 2H, -PhH), 5.40 (m, 7H, -C=CH-), 4.90 (m, 7H, -COOCH-), 2.50 (d, 14H, $-CH_2$-β-COO), 2.1-0.85 (m, 266H, $-CH_3$, $-CH_2$, -CH), 0.65 (s, 21H, $-CH_3$). ^{13}C NMR (75MHz, $CDCl_3$): δ(ppm) 11.95, 18.8, 19.4, 21.15, 22.65, 22.9, 23.9, 24.4, 27.8, 28.1, 28.3, 31.95, 32.0, 35.9, 36.3, 36.7, 37.1, 38.1, 39.6, 39.8, 42.4, 50.1, 56.3, 56.8 (C_{chol}), 75.4 (C-α-O-C=O), 76.1 (C-α-O-C=O), 91.1 (C1, C40), 94.4 (C≡C), 123.0 (C4, C37), 123.1 (CH=C_{chol}), 123.4 (C10, C16, C22, C25), 123.5 (C7, C13, C19, C28, C34), 132.9 (C8, C18, C20, C29, C33), 133.8 (C11, C15, C23, C26, C36), 134.2 (C12, C14, C24, C27, C35), 134.7 (C3, C38), 136.0 (C9, C17, C21, C30, C32) 139.4 (CH=C_{chol}), 139.5 (C6, C41), 139.6 (C5, C42), 141.5 (C2, C39), 164.8 (O=C-O), 165.4 (O=C-O). Anal. Calcd (%) for $C_{250}H_{336}I_2O_{14}$: C, 78.62; H, 8.87. Found: C, 78.14; H, 8.55. UV($CHCl_3$): λ_{max}(372 nm), ε(1.374 X 10^5 L mol^{-1} cm^{-1}). Fluorescence ($CHCl_3$): λ_{max}= 417 nm. Raman ν_{Max} (powder, laser 830nm)/cm^{-1} 2198 (-C≡C-).

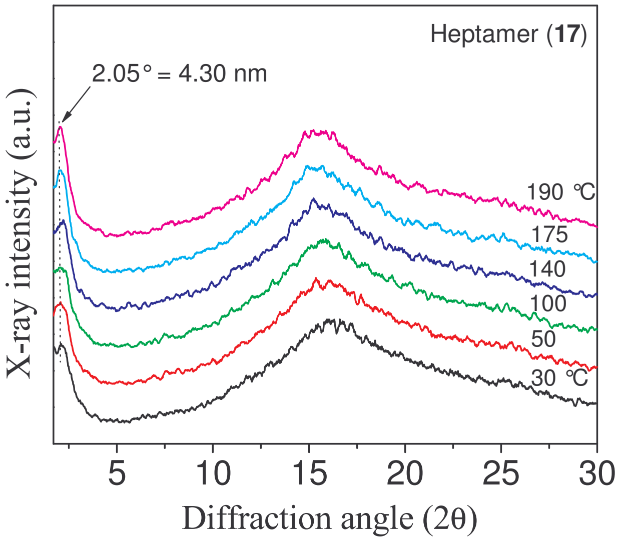
Homopolymer (*Br*-nPEBzCol). This compound was synthesized applying the same procedure to prepare **5. 8** (0.3g, 0.463mmol)**, 10** (0.249g, 0.463mmol), bis(triphenylphosphine) palladium (II) dichloride (16mg, 0.023mmol) and cuprous iodide (1.3mg, 0.007mmol) in 50 ml of Et_3N were reacted over night at 70°C under nitrogen. The ammonium salt was filtered off and washed with THF. Then, the solvents were evaporated until get a pasty material. The crude product was precipitated in methanol (25 mL) containing 2.0 % mol (12 mg) of sodium diethyldithiocarbamate in order to eliminate all the rest of the catalyst, centrifuged and dissolved in the minimum $CHCl_3$ and re-precipitated in clean methanol for another two precipitation cycles. Then, passed by preparative GPC chromatography (Biorads, Bio-Beds SX1, chloroform) to ffinally be filtered and stored in refrigeration in $CHCl_3$. ^{1}H NMR (300 MHz, CDCl3): δ(ppm): 8.15 (bm, Ar-H), 8.0 (bd, Ar-H), 7.4-7.7 (bm, Ar-H), 5.40 (bs, CH=C_{chol}), 4.90 (bm, CH-α-O-C=O), 2.50 (bd, CH_2-β-O-C=O), 0.85-2.1 (bm, CH_3, CH_2, CH), 1.00 (CH_3-Cquat), 0.90 (d, *gem*-CH_3), 0.85 (d, *gem*-CH_3), 0.65 (s, CH_3-Cquat). Anal. Found (%) C, 73.93; H, 9.18. UV($CHCl_3$): λ_{max}(380 nm), ε(1.079 X 10^5 L mol^{-1} cm^{-1}). Fluorescence ($CHCl_3$): λ_{max}= 422 n. Raman ν_{Max} (powder, laser 830nm)/cm^{-1} 2199 (-C≡C-).

II. TGA

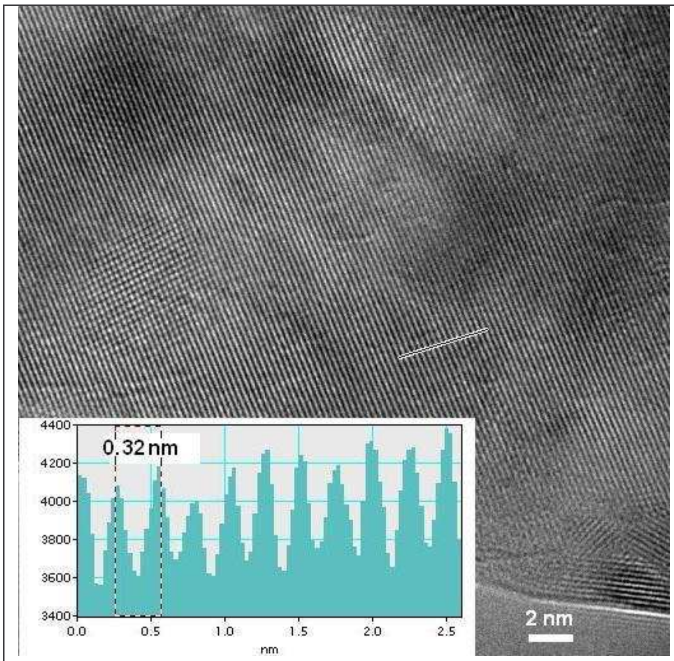


III. Temperature dependant X-ray diffraction patterns of oligomers.

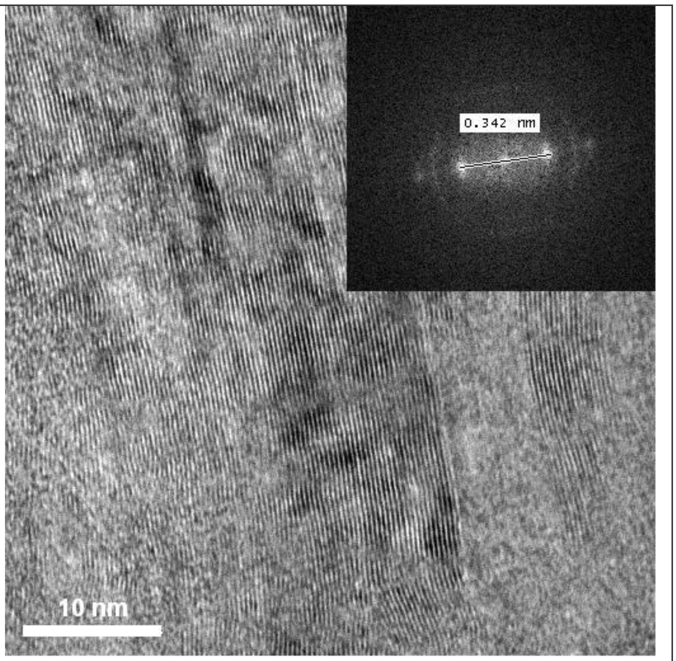




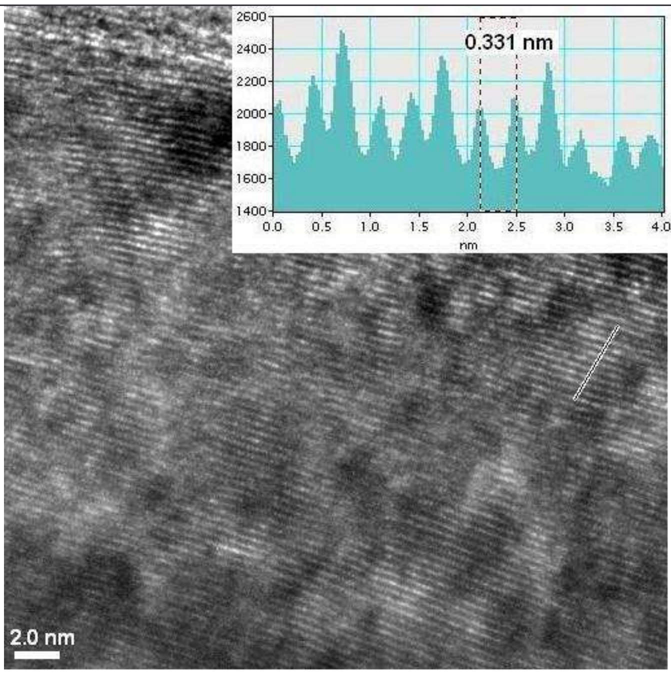
IV. HRTEM images



Pentamer 14

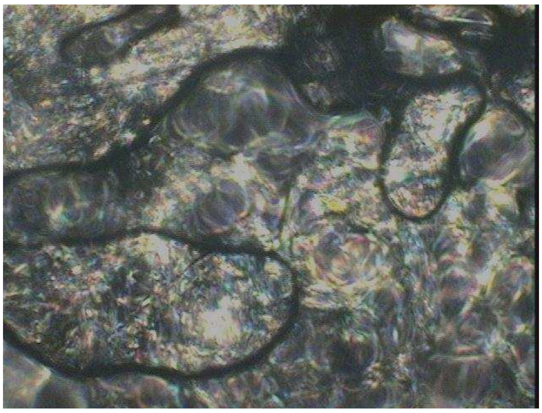


Heptamer 17

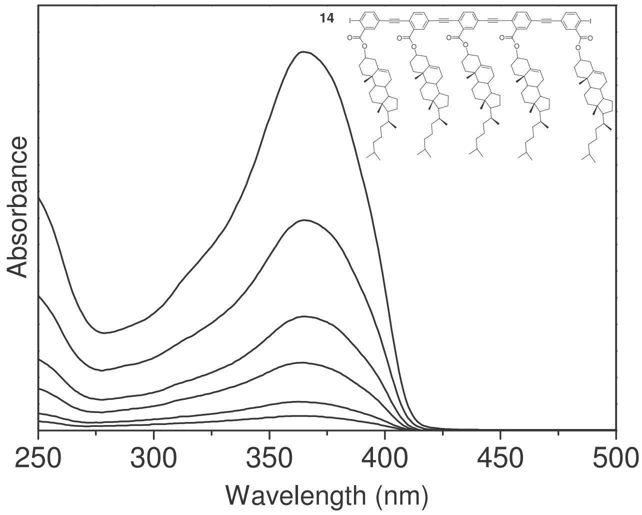


Polymer Br-nPEBzCol

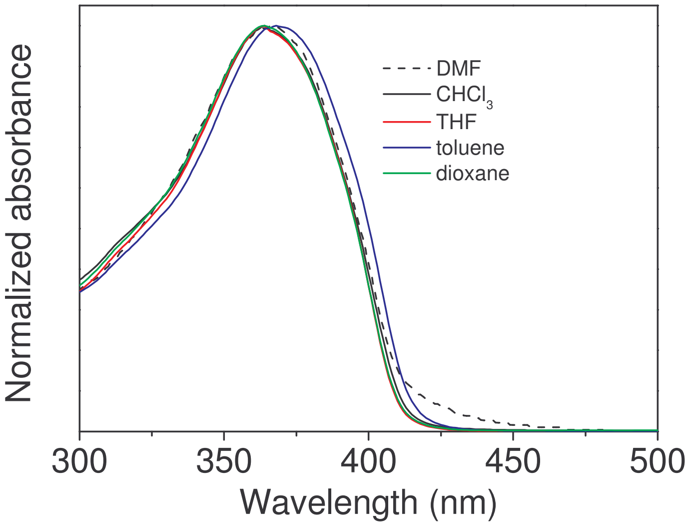
V. Texture image of (cholesteryl) 2,5-dibromobenzoate at 165-170 °C (8).



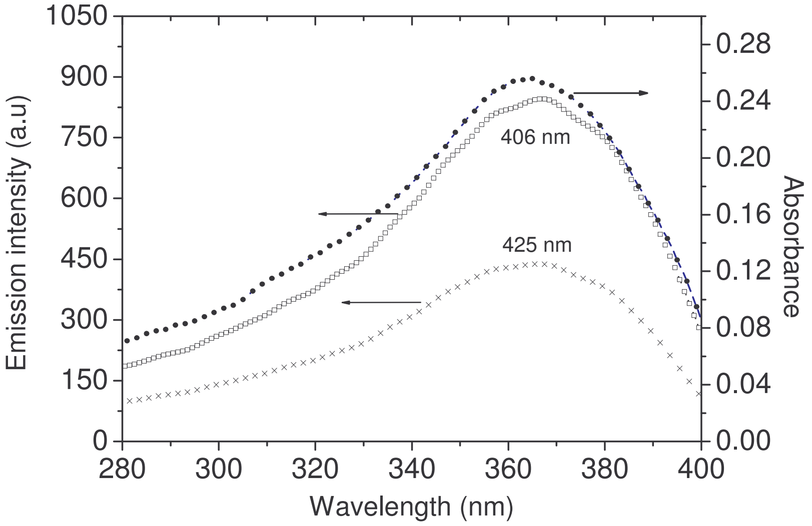
VI. Optical spectra in solution



UV-Vis spectra of cholesteryl iodine terminated pentamer **14** in chloroform at different concentration, up to $1.07*10^{-5}$ M.

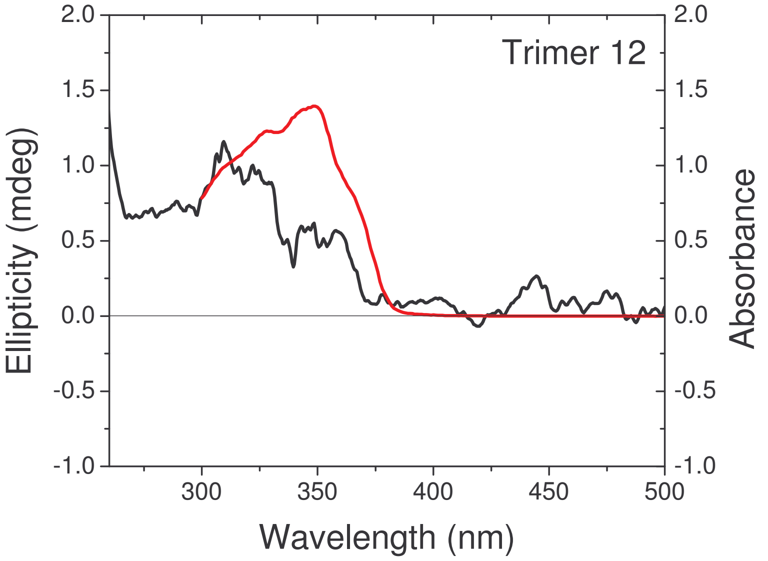


UV-Vis spectra of cholesteryl iodine terminated pentamer **14** in different solvents.

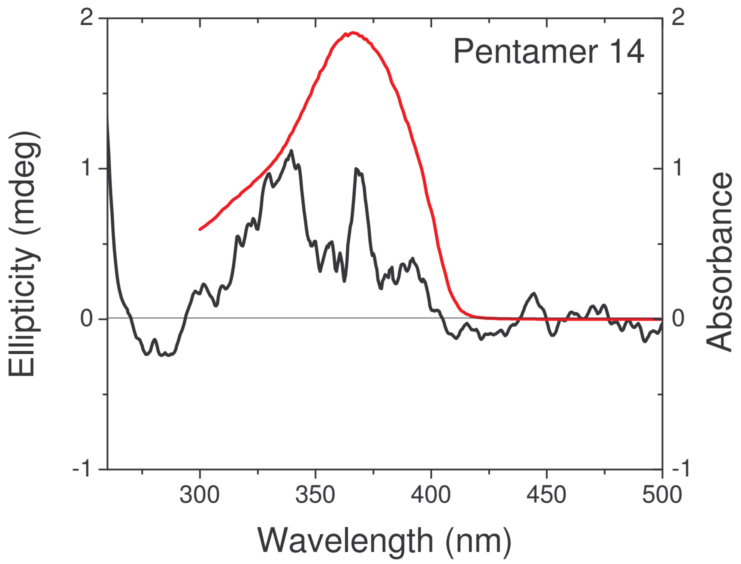


Excitation spectra (solid lines) recorded at 406 nm (top) and 425 nm (bottom) and UV-Vis spectra (circules) of colesteryl iodine pentamer.

VII. Circular dichroism

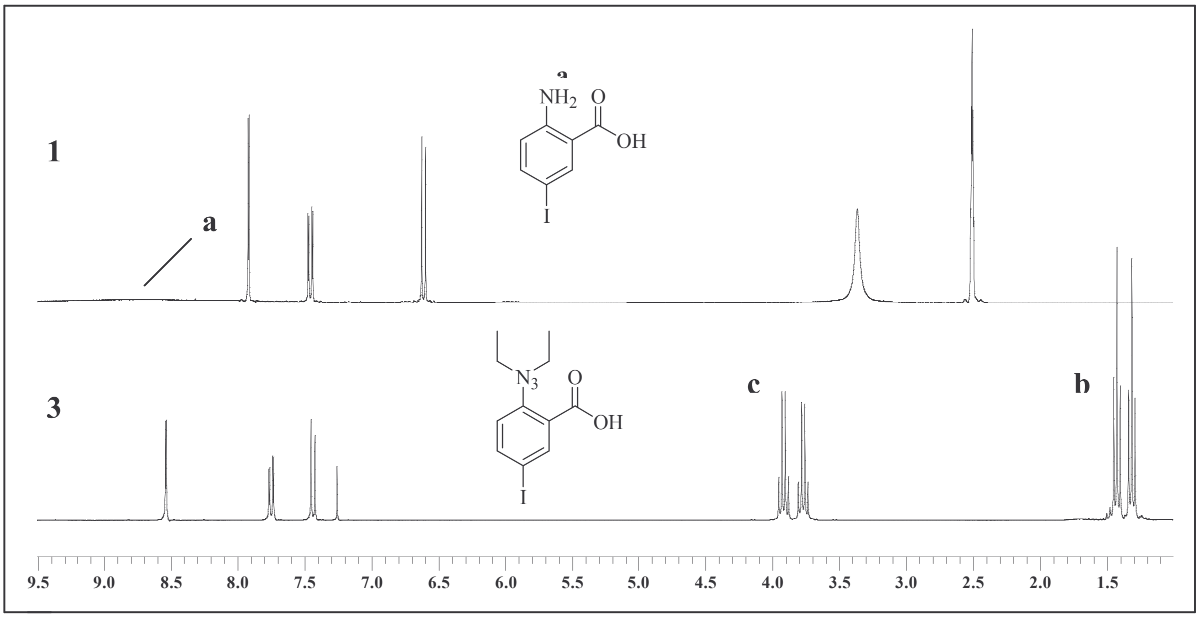


Black curve: circular dichroism spectrum of 210 µM trimer **12** dissolved in chloroform; Red curve: ground state absorption spectrum.

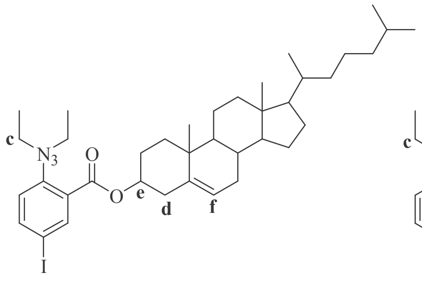


Black curve: circular dichroism spectrum of 93 μM pentamer **14** dissolved in chloroform; Red curve: ground state absorption spectrum.

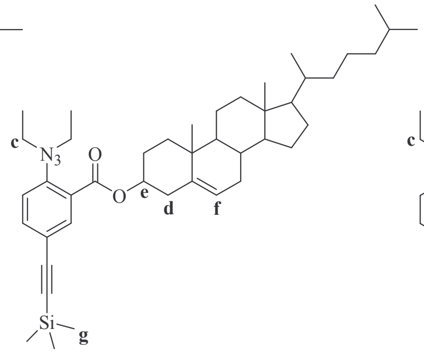
VIII. Selected NMR spectra



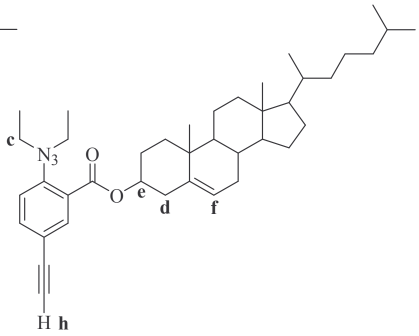
^{1}H NMR spectra of 2-amino-5-iodobenzoic acid **1** in DMSO-d_6 and of 2-(3,3-diethyltriazene)-5-iodobenzoic acid **3** in $CDCl_3$.



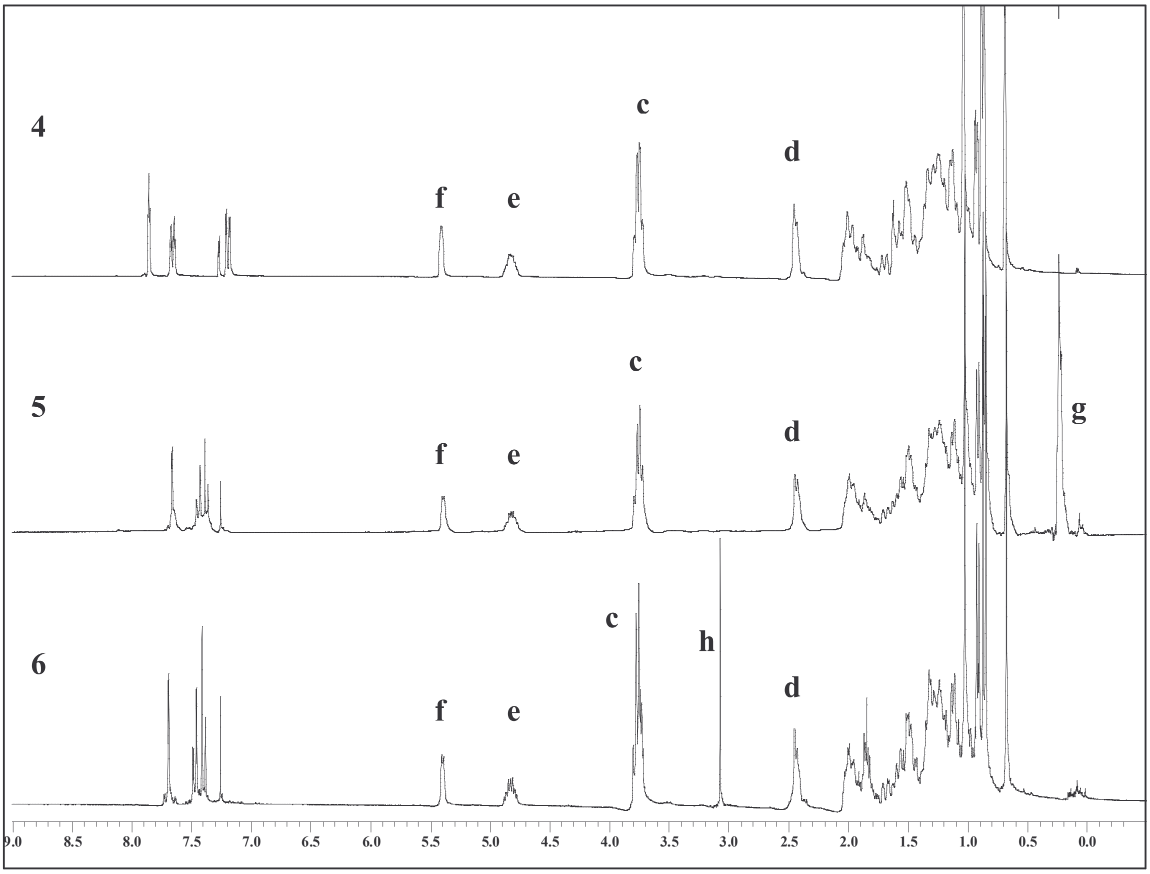
4



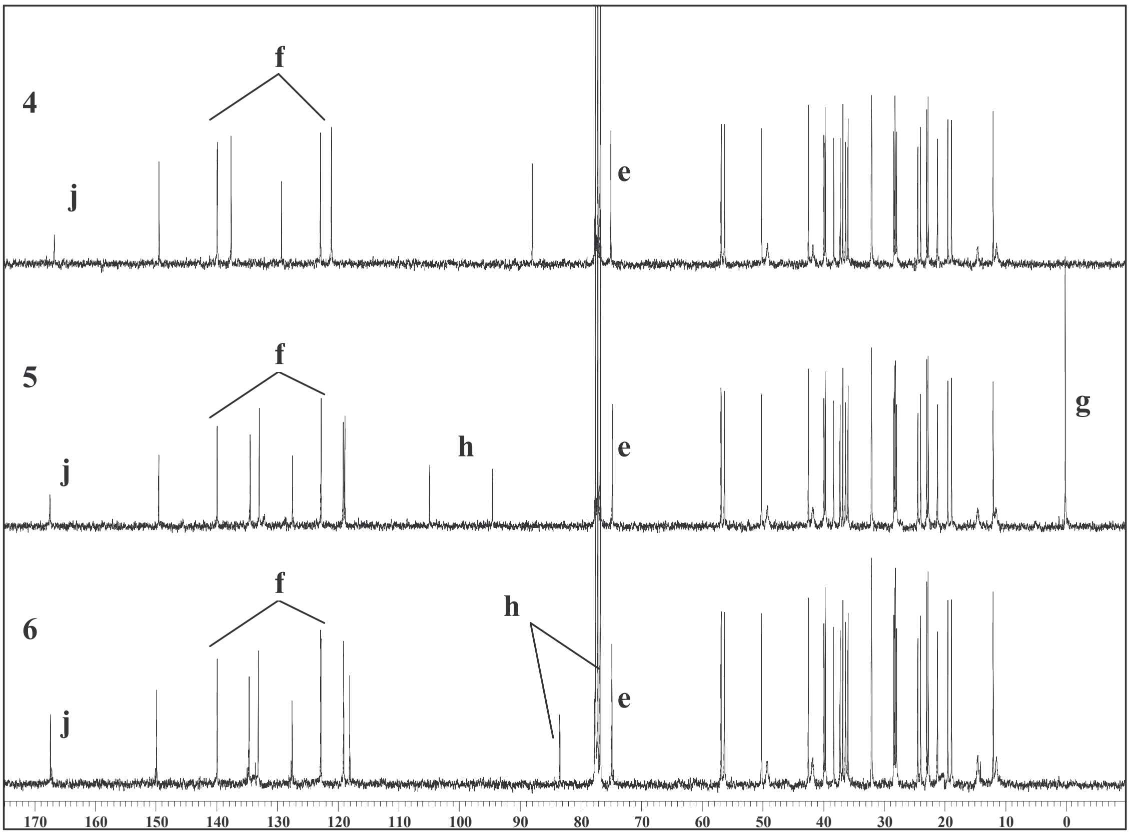
5



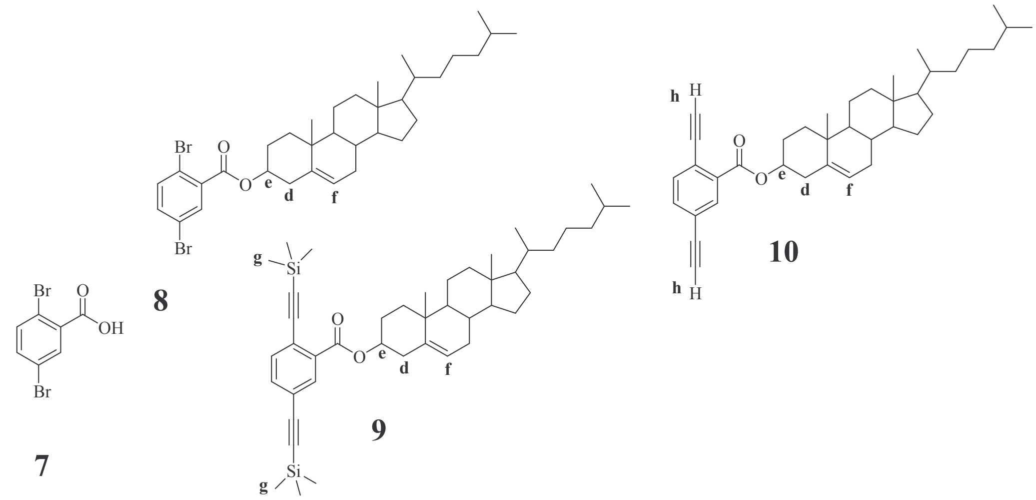
6



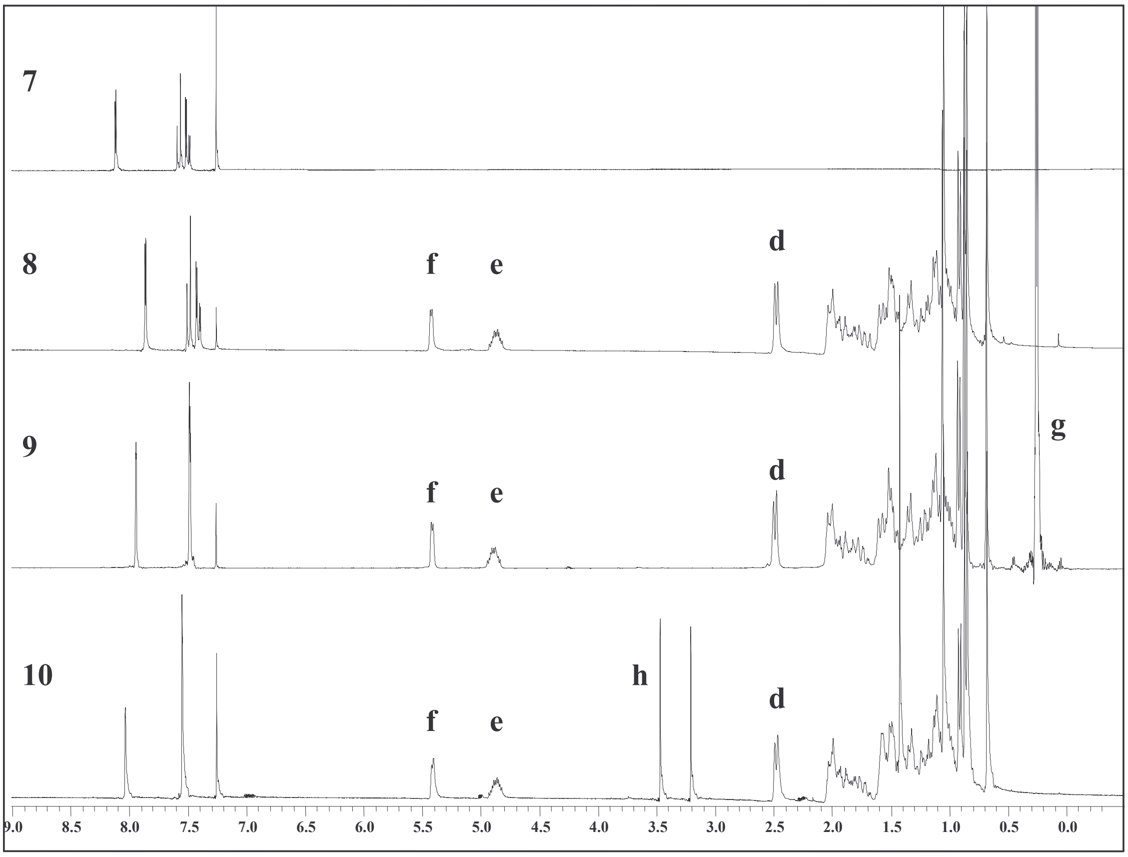
^{1}H NMR spectra of 2-[(3,3-diethyltriazene)]-5-[iodo] (cholesteryl) benzoate **4**, 2-[(3,3-diethyltriazene)]-5-[(trimethylsilyl)ethynyl] (cholesteryl) benzoate **5** and 2-[(3,3-diethyltriazene]-5-[ethynyl] (cholesteryl) benzoate **6** in $CDCl_3$.



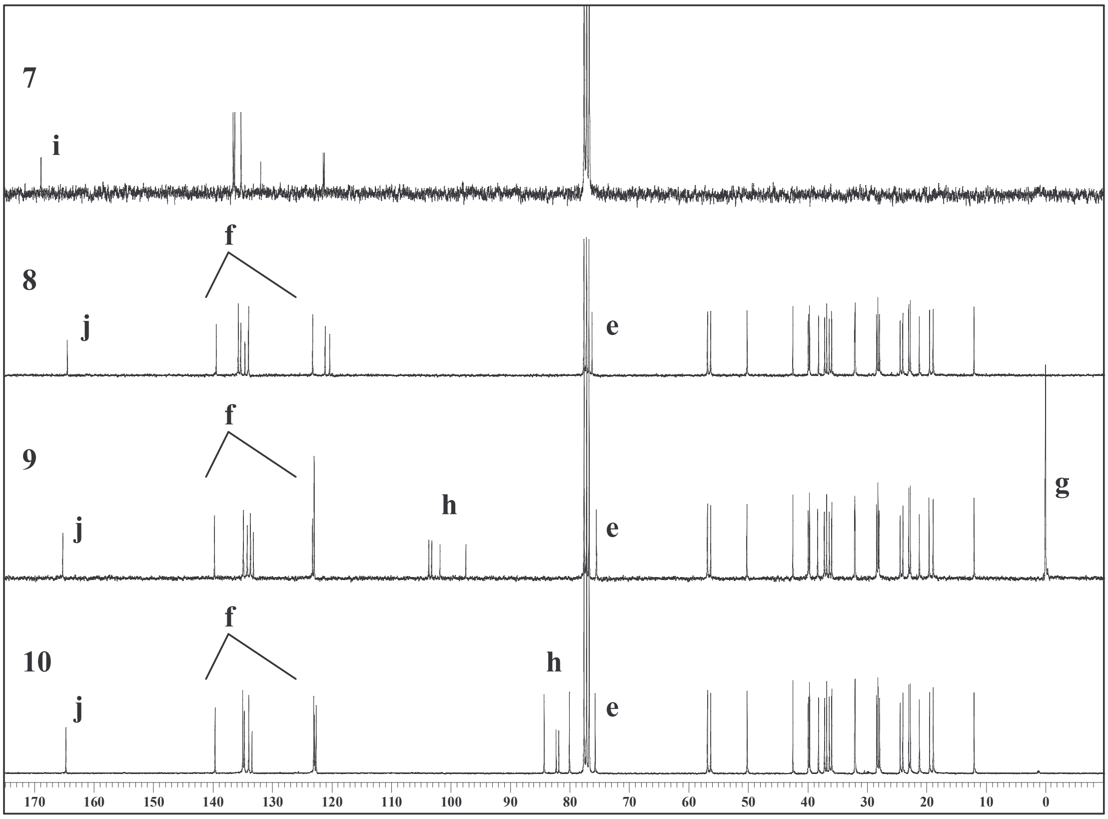
^{31}C NMR spectra of 2-[(3,3-diethyltriazene)]-5-[iodo] (cholesteryl) benzoate **4**, 2-[(3,3-diethyltriazene)]-5-[(trimethylsilyl)ethynyl] (cholesteryl) benzoate **5** and 2-[(3,3-diethyltriazene]-5-[ethynyl] (cholesteryl) benzoate **6** in $CDCl_3$.



7 **8** **9** **10**



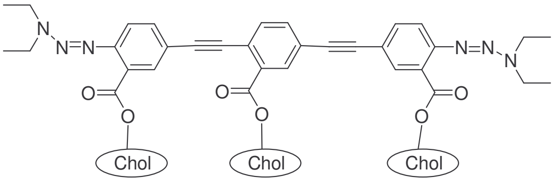
^{1}H NMR spectra of 2,5-dibromo benzoic acid **7**, (cholesteryl) 2,5-dibromobenzoate **8**, 2,5-di[(trimethylsilyl) ethynyl] (cholesteryl) benzoate **9** and of (cholesteryl) 2,5-diethynyl benzoate **10** in $CDCl_3$.

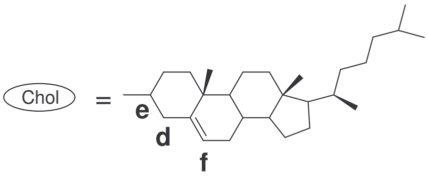


^{31}C NMR spectra spectra of 2,5-dibromo benzoic acid **7**, (cholesteryl) 2,5-dibromobenzoate **8**, 2,5-di[(trimethylsilyl) ethynyl] (cholesteryl) benzoate **9** and of (cholesteryl) 2,5-diethynyl benzoate **10** in CDCl$_3$.

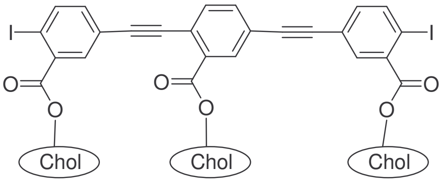
.

11

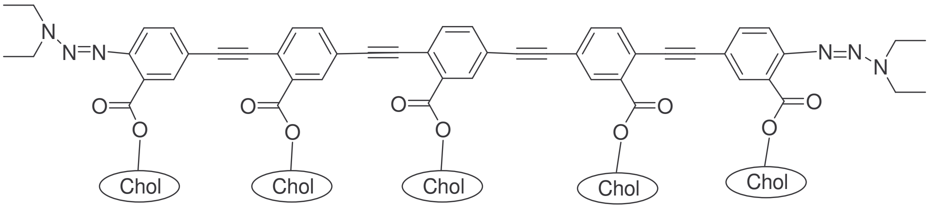




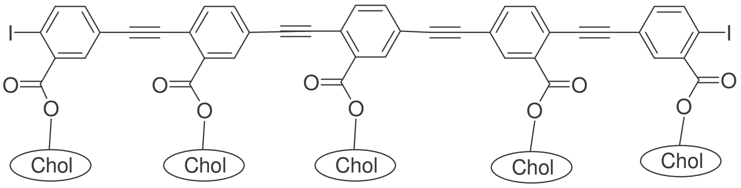
12



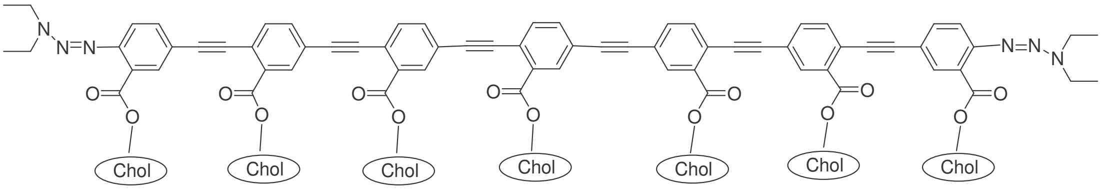
13



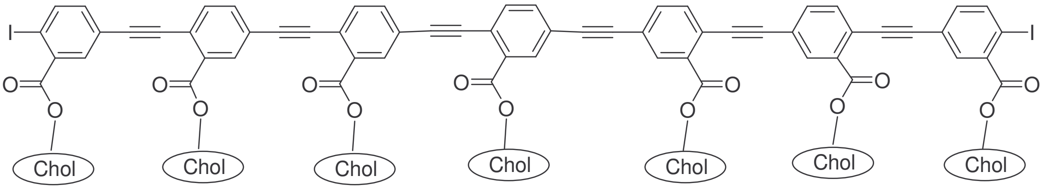
14

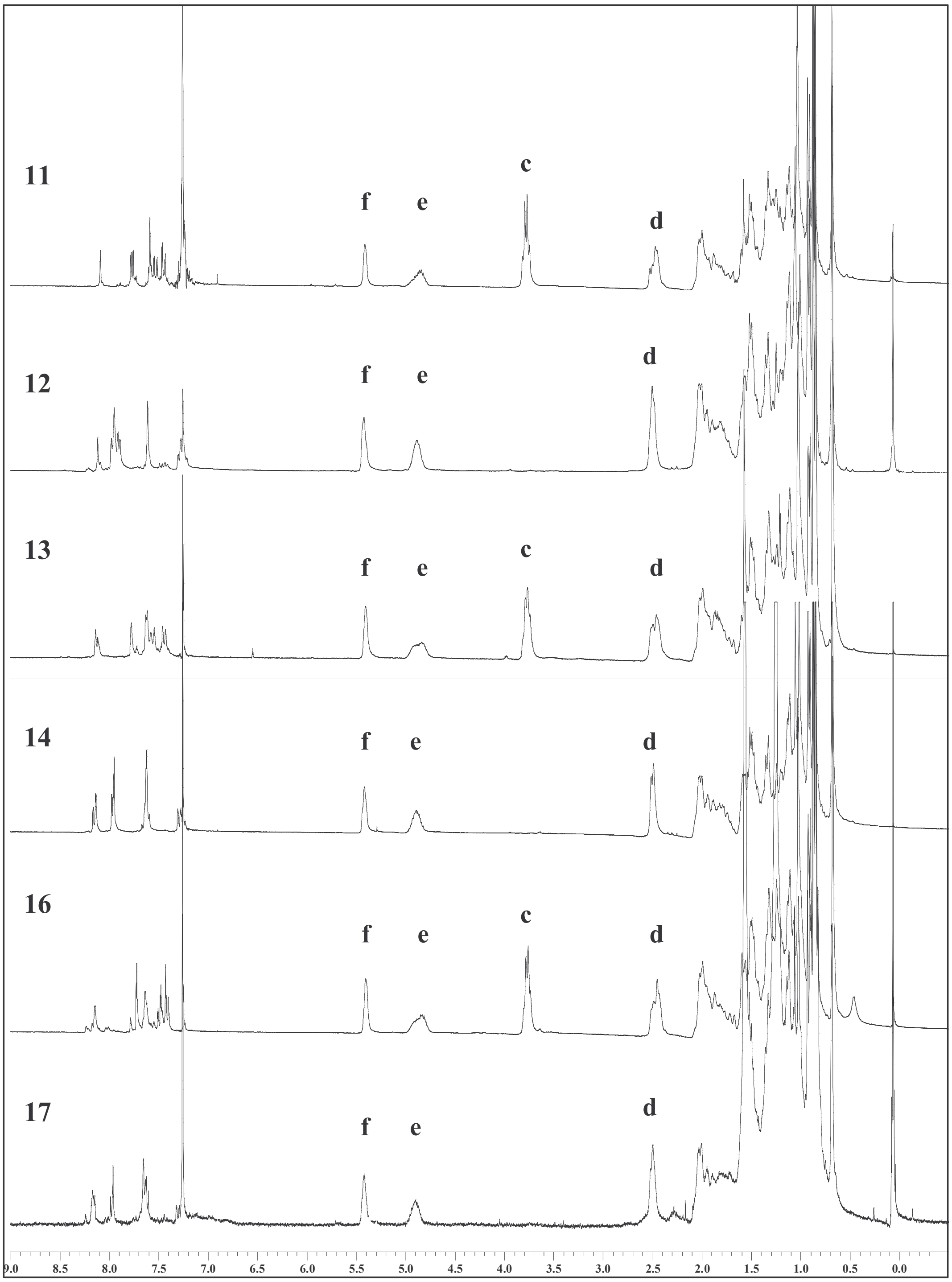


16

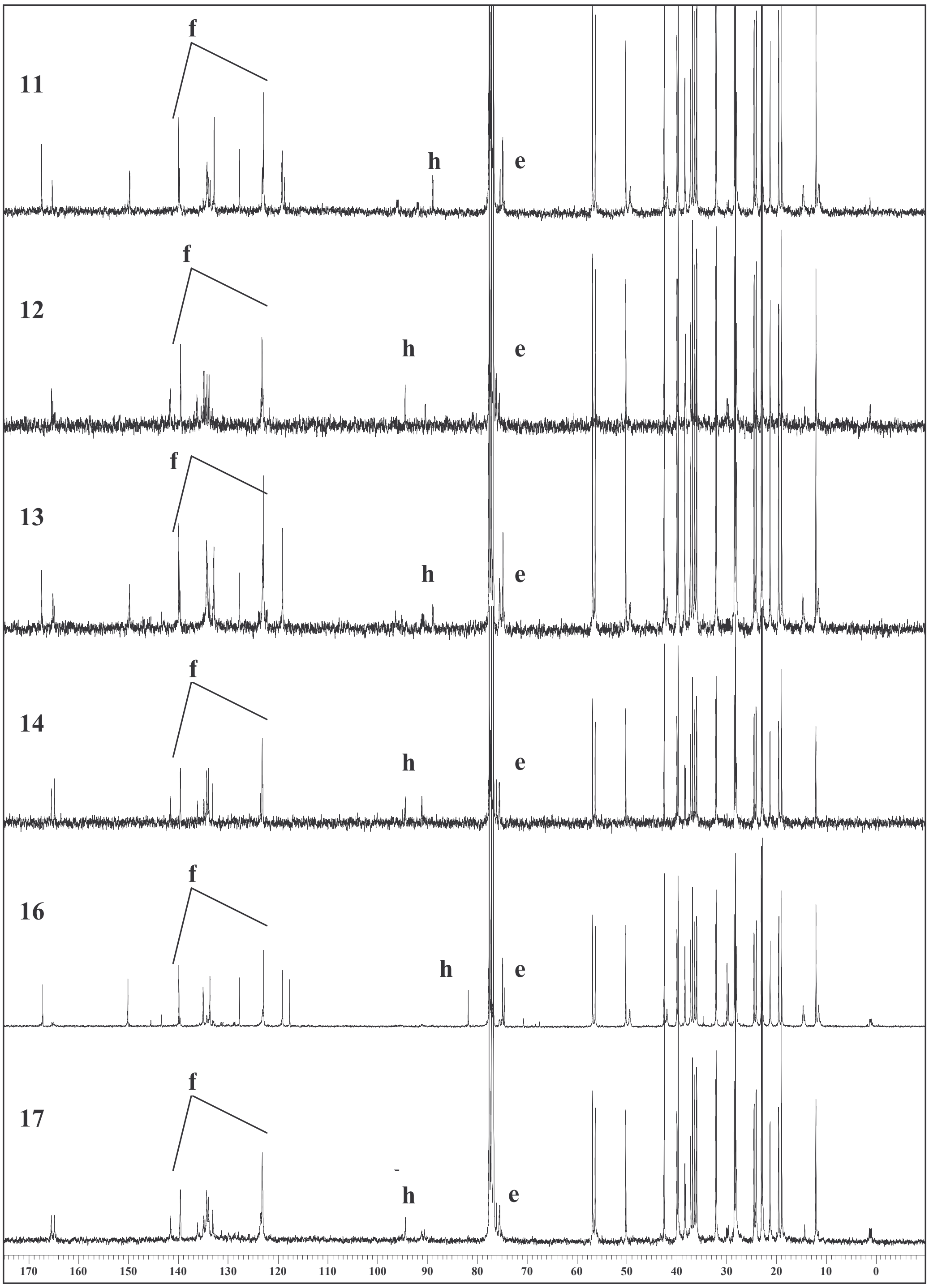


17

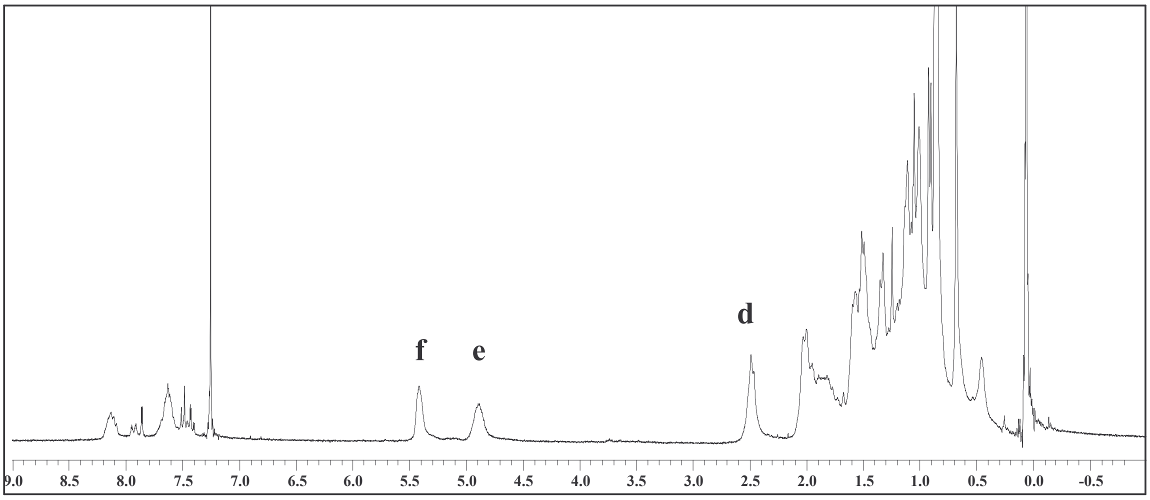




^{1}H NMR spectra of triazene terminated trimer **11**, iodine terminated trimer **12**, triazene terminated pentamer **13**, iodine terminated pentamer **14**, triazene terminated heptamer **16** and iodine terminated heptamer **17** in $CDCl_3$.



^{13}C NMR spectra of triazene terminated trimer **11**, iodine terminated trimer **12**, triazene terminated pentamer **13**, iodine terminated pentamer **14**, triazene terminated heptamer **16** and iodine terminated heptamer **17** in $CDCl_3$.



^{1}H NMR spectra of the polymer ***Br*-nPEBzCol** in $CDCl_3$.