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SUPPORTING INFORMATION

Title: New H-Bonded Complexes and Their Supramolecular Liquid-Crystalline Organizations
Author(s): Ana Pérez, Nélida Gimeno, Francisco Vera, M. Blanca Ros,* José Luis Serrano, M. Rosario De la Fuente
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Synthetic procedures.

Unless otherwise indicated, all materials were purchased from Aldrich, Fluka and Acros. THF was dried by refluxing over sodium under an argon atmosphere and freshly distilled before use. Dichloromethane was dried by refluxing over calcium hydride under an argon atmosphere and was freshly distilled prior to use. Acids 2 and 3 (see Schemes 6 and 7) were synthesized according to methods described in the literature.[5]

Synthesis of 1,3-(trans-4-pyridin-vinyl)benzene (III). This compound was prepared by an adaptation of a previously reported method.[16] Yield: 0.205 g of yellow solid (45%). R_f 0.15 (1/1, dichloromethane/ethyl acetate): mp: 208 ºC (lit.[17] 211-212 ºC). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.08 (d, J = 16.4 Hz, 2H); 7.31-7.44 (m, 7H); 7.50-7.53 (m, 2H); 7.69 (s, 1H); 8.61 (d, J = 8.0 Hz, 4H). ^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm): 120.9, 125.7, 126.7, 127.2, 129.4, 132.6, 136.8, 144.4, 150.3.IR (KBr): 1591, 1412, 970 cm^{-1}. MS (FAB+) m/z: 285. Anal. for $C_{20}H_{16}N_2$ (284.35): Calcd. 84.48% C, 5.67% H, 9.85% N; found: 84.09% C, 5.82% H, 9.78% N.

Synthesis of 1,3-bis(4-formylbenzoyloxy)benzene (1). This compound was prepared by adapting a previously reported method. [17] Yield: 3.29 g of white solid (40%). R_f 0.38 (dichloromethane) mp: 194 ºC. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 7.19 (s, 1H); 7.23 (d, J = 8.1 Hz, 2H); 7.51 (t, J = 8.1 Hz, 1H); 8.02 (d, J = 8.1 Hz, 2H); 8.35 (d, J = 8.1 Hz, 2H); 10.13 (s, 2H). IR (NaCl): 1737, 1690, 1461, 1262, 1139 cm^{-1}.

Synthesis of 1,3-bis(trans-4´-stilbazole-carboxyloxy)benzene (IV). A mixture of 3-bis(4-formylbenzoyloxy)benzene (1) (0.500 g, 1.33 mmol), 4-picoline (0.249 g, 2.67 mmol) and acetic anhydride (2 mL) was heated at 120 ºC for 48 h under an argon atmosphere. The reaction mixture was cooled and poured over cold water. The resulting solid was filtered off and washed several times with cold water. The crude product was purified by flash chromatography using dichloromethane/ethyl acetate (8/2) (v/v) as eluent and crystallized from ethyl acetate. Yield: 0.279 g of yellow solid (40%). R_f 0.1 (1:1, dichloromethane: ethyl acetate) mp: 192 ºC. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 7.14-7.22 (m, 6H); 7.33 (s, 2H); 7.38-7.41 (m, 6H); 7.50 (t, J = 9.0 Hz, 1H); 7.66-7.69 (m, 5H); 8.22 (d, J = 8.7 Hz, 4H). ^{13}C NMR (300 MHz, $CDCl_3$) δ ppm: 115.7, 119.2, 121.0, 127.0, 129.0, 129.8, 129.9, 130.7, 131.8, 141.3, 143.9, 150.3, 151.4, 164.3. IR (KBr): 1728, 1595, 1258, 1129, 1066 cm^{-1}. MS (FAB+) m/z: 525. Anal. for $C_{34}H_{24}N_2O_4$ (524.55): calcd.: 77.85% C, 4.61% H, 5.34% N; found: 77.53% C, 4.68% H, 5.18% N.

Synthesis of 3-((4-n-tetradecyloxybenzoyloxy)benzoyloxy)pyridine (V). To a solution of 3-hydroxypyridine (0.105 g, 1.1 mmol) in distilled dichloromethane (20 mL) was added 4-n-tetradecyloxybenzoyloxybenzoic acid (0.500 g, 1.1 mmol) and N,N-dimethylaminopyridine (DMAP) (0.013 g, 0.11 mmol) under an argon atmosphere. The mixture was cooled in a water-ice bath and after 30 min dicyclohexylcarbodiimide (DCC) (10.227 g, 1.1 mmol) was added. The reaction mixture was stirred for 24 h at room temperature. After this time, the resulting white solid was filtered off and the solvent evaporated. The crude product was purified by flash chromatography using dichloromethane as eluent and crystallized from ethyl acetate. Yield: 0.290 g of a white solid (50%). R_f 0.66 (8/2, dichloromethane/ethyl acetate) mp: C 114 ºC SmA 148 ºC I. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm:0.90 (t, J = 6.4 Hz, 3H); 1.29-1.50 (m, 22H); 1.83-1.87 (m, 2H); 4.08 (t, J = 6.4 Hz, 2H); 7.01 (d, J = 8.8 Hz, 2H); 7.40-7.44 (m, 3H); 7.64 (dd, J = 1.6 Hz, J = 8.4 Hz, 1H); 8.16 (d, J = 8.8 Hz, 2H); 8.32 (d, J = 8.8 Hz, 2H); 8.56 (d, J = 4.8 Hz, 1H); 8.59 (d, J = 1.6 Hz, 1H). ^{13}C-NMR (400 MHz, $CDCl_3$) δ ppm:14.1, 22.7, 26.0, 29.1, 29.4, 29.5, 29.6, 29.7, 31.9, 68.4, 114.5, 119.9, 120.9, 122.2, 124.0, 126.1, 129.4, 131.9, 132.5, 132.4, 143.6, 147.1, 147.6, 155.7, 163.8, 164.2. IR (KBr): 1743, 1732, 1607, 1471, 1210, 1067 cm^{-1}. MS (FAB+) m/z: 317, 532. Anal. for $C_{33}H_{41}NO_5$ (531.67): Calcd.: 74.55% C, 7.77% H, 2.63% N, found: 74.33% C, 7.82% H, 2.67% N.

Synthesis of 4-aminophenyl 4-n-tetradecyloxybenzoate (4).

i) 4-nitrophenyl 4-n-tetradecyloxybenzoate. A solution of 4-n-tetradecyloxybenzoic acid (4.0 g, 11.96 mmol), 4-nitrophenol (1.68 g, 11.96 mmol), DMAP (0.02 g, 0.12 mmol) and DCC (2.74 g, 13.15 mmol) in distilled dichloromethane (126 mL) was stirred and cooled in a water-ice bath under an argon atmosphere. After 30 min the water-ice bath was removed and the reaction mixture was stirred for 21 h at room temperature. After this time, the reaction mixture was filtered through a pad of silica and washed with dichloromethane. The solvent was evaporated and the crude product was crystallized from ethanol. Yield: 1.68 g of a yellow solid (81%). Mp: C 66 ºC SmA 85 ºC I. R_f = 0.70 (dichloromethane). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm): 0.88 (t, 3H, J = 6.8 Hz), 1.25-1.56 (m, 22H), 1.79-1.86 (m, 2H), 4.05 (t, 2H, J = 6.8 Hz), 6.98 (d, 2H, J = 8.9 Hz), 7.40 (d, 2H, J = 9.1 Hz), 8.13 (d, 2H, J = 8.8

Hz), 8.31 (d, 2H, J = 9.1 Hz). IR (KBr): 2916, 2849, 1732, 1609, 1597, 1528, 1514, 1349, 1272, 1221, 1175 cm^{-1}. Anal. for $C_{27}H_{37}O_5N$ (455.58): calcd.: 71.18% C, 8.18% H, 3.07% N; found: 71.00% C, 8.15% H, 3.15% N.

ii) Synthesis of 4-aminophenyl 4-n-tetradecyloxybenzoate (4). To a mixture of 4-nitrophenyl 4-n-tetradecyloxybenzoate (3.0 g, 6.58 mmol), ethanol (73 mL) and cyclohexene (21 mL) was added $Pd(OH)_2/C$ (0.41 g) under an argon atmosphere. The reaction mixture was protected from the light and was heated under reflux for 6 h. After this time the reaction mixture was allowed to cool to room temperature. The reaction mixture was filtered through a pad of Celite® and washed with ethyl acetate. The solvent was evaporated under vacuum and the crude product was purified by column chromatography (SiO_2, hexane:ethyl acetate, 7:3). Yield: 1.81 g of a yellow solid (64%). Mp 92 ºC. R_f = 0.22 (hexane: ethyl acetate, 7:3). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm): 0.88 (t, 3H, J = 6.5 Hz), 1.25-1.50 (m, 22H), 1.78-1.85 (m, 2H), 3.60-3.77(m, < 2H), 4.05 (t, 2H, J = 6.5 Hz), 6.70 (d, 2H, J = 9.1 Hz), 6.93-6.97 (m, 4H), 8.12 (d, 2H, J = 9.1 Hz). IR (KBr): 3440, 3410, 3340, 2917, 2849, 1729, 1606, 1512, 1203, 1170 cm^{-1}. Anal. for $C_{27}H_{39}O_3N$ (425.59): calcd.: 76.19% C, 9.24% H, 3.29% N; found: 76.04% C, 9.24% H, 3.29% N.

Synthesis of 3-(4-(4-n-tetradecyloxybenzoyloxy)phenyliminomethyl)pyridine (VI). To a solution of 4-aminophenyl 4-n-tetradecyloxybenzoate (0.56 g, 1.31 mmol) and 3-pyridinecarboxaldehyde (0.18 g, 1.70 mmol) in absolute ethanol (25 mL) were added a few drops of glacial acetic acid. The reaction mixture was heated under reflux for 5 h and allowed to cool to room temperature. A precipitate formed and this was filtered off and then purified by crystallization from ethanol. Yield: 0.48 g of a solid (72%). Mp: C 87 ºC SmA 136 ºC N 142 ºC I. R_f = 0.5 (ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm): 0.88 (t, 3H, J = 6.7 Hz). 1.27-1.47 (m, 22H), 1.79-1.86 (m, 2H), 4.05 (t, 2H, J = 6.5 Hz), 6.97 (d, 2H, J = 6.9 Hz), 7.24-7.31 (m, 4H), 7.41-7.44 (m, 1H), 8.15 (d, 2H, J = 7.0 Hz), 8.29-8.32 (m, 1H), 8.53 (s, 1H), 8.71-8.72 (m, 1H), 9.03(s, 1H). IR (KBr): 2917, 2849, 1734, 1609, 1511, 1292, 1257, 1085, 759 cm^{-1}. Anal. for $C_{33}H_{42}O_3N_2$ (514.69): calcd.: 77.01% C, 8.22% H, 5.44% N; found: 76.89% C, 8.20% H, 5.48% N.

Synthesis of 4-(4-n-tetradecyloxybenzoyloxy)benzaldehyde (5). 4-Hydroxybenzaldehyde (0.57 g, 4.56 mmol) was dissolved in distilled dichloromethane (48 mL). The solution was purged with argon and cooled in a water-ice bath. 4-n-tetradecyloxybenzoic acid (1.53 g, 4.56 mmol), N,N-dimethylaminopyridine (DMAP) (0.006 g, 0.05 mmol) and dicyclohexylcarbodiimide (DCC) (1.05 g, 5.02 mmol) were added. After 30 min, the water-ice bath was removed. The reaction mixture was stirred for 24 h at room temperature. After this time, the reaction mixture was filtered through a pad of silica and washed with dichloromethane. The solvent was evaporated and the white solid was crystallized from ethanol. Yield: 1.54 g of a white solid (77%). Mp: C 57 ºC SmA 77 ºC I. R_f = 0.72 (hexane: ethyl acetate, 7:3). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm): 0.88 (t, 3H, J = 6.3 Hz), 1.26-1.45 (m, 22H), 1.78-1.86 (m, 2H), 4.05 (t, 2H, J = 6.2 Hz), 6.98 (d, 2H, J = 7.5 Hz), 7.39 (d, 2H, J = 7.2 Hz), 7.98 (d, 2H, J = 7.2 Hz), 8.13 (d, 2H, J = 7.4 Hz), 10.02 (s,1H). IR (KBr): 2916, 2850, 1724, 1698, 1608, 1514, 1471, 1284, 1266, 1228, 1174 cm^{-1}.

Synthesis of 3-(4-(4-n-tetradecyloxybenzoyloxy)benzylimino)pyridine (VII). To a solution of 4-(4-n-tetradecyloxybenzoyloxy)benzaldehyde (0.51 g, 1.16 mmol) and 3-aminopyridine (0.14 g, 1.52 mmol) in ethanol (20 mL) were added a few drops of glacial acetic acid. The reaction mixture was heated under reflux for 8 h and allowed to cool to room temperature. A precipitate was formed and this was filtered off and then purified by crystallization from ethanol. Yield: 0.38 g of a yellow solid (65%). Mp: C 96 ºC SmA 146 ºC I. R_f = 0.47 (ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm): 0.88 (t, 3H, J = 6.7 Hz), 1.27-1.47 (m, 22H), 1.79-1.86 (m, 2H), 4.05 (t, 2H, J = 6.5 Hz), 6.98 (d, 2H, J = 8.8 Hz), 7.32-7.37 (m, 3H), 7.52-7.55 (m, 1H), 7.99 (d, 2H, J = 8.5 Hz), 8.15 (d, 2H, J = 8.8 Hz), 8.48-8.53 (m, 3H). IR (KBr): 2917, 2849, 1723, 1630,1604, 1511, 1463, 1264, 1206, 1171, 1073 cm^{-1}. Anal. for $C_{33}H_{42}O_3N_2$ (514.69): calcd.: 77.01% C, 8.22% H, 5.44% N; found: 76.88% C, 8.22% H, 5.45% N.

Synthesis of 4-(4-n-tetradecyloxybenzoyloxy)phenol (6).

i) Synthesis of 4-(benzyloxy)phenyl 4-n-tetradecyloxybenzoate. To a solution of 4-benzyloxyphenol (0.600 g, 2.99 mmol) in distilled dichloromethane (50 mL) was added 4-tetradecyloxybenzoic acid (1.00 g, 2.99 mmol) and N,N-dimethylaminopyridine (DMAP) (0.037 g, 0.029 mmol) under an argon atmosphere. The mixture was cooled in a water-ice bath and after 30 min dicyclohexylcarbodiimide (DCC) (0.617 g, 2.99 mmol) was added. The reaction mixture was stirred for 24 h at room temperature. After this time, the white solid was filtered off and the solvent evaporated. The crude product was purified by flash chromatography using dichloromethane as eluent. Yield: 1.12 g of a white solid (73%). Rf 0.77 (hexanes: ethyl acetate 7:3). Mp: 110 ºC. ^{1}H-NMR (400

MHz, $CDCl_3$) δ (ppm): 0.88 (t, J = 6.4 Hz, 3H); 1.26-1.47 (m, 22H); 1.77-1.85 (m, 2H); 4.05 (t, J = 6.4 Hz, 2H); 5.08 (s, 2H); 6.95 (d, J = 8.8 Hz, 2H); 7.00 (d, J = 8.8 Hz, 2H); 7.44 (d, J = 8.8 Hz, 2H); 7.33-7.45 (m, 5H); 8.12 (d, J = 8.8 Hz, 2H). IR (Nujol, NaCl): 1723, 1607, 1585, 1462, 1167 cm^{-1}.

ii) Synthesis of 4-(4-n-tetradecyloxybenzoyloxy)phenol (6). $Pd(OH)_2/C$ (20%) (0.180 g, 10% weight) was added over a solution of 4-(benzyloxy)phenol 4-n-tetradecyloxybenzoate (1.80 g, 3.52 mmol) in ethanol (50 mL) and cyclohexene (14 mL), and the mixture was heated under reflux for 2 h under an argon atmosphere. The solution was allowed to cool, filtered through a pad of Celite® and washed with THF. The organic solution was evaporated to yield a white solid, which was recrystallized from ethanol. Yield: 1.20 g of a white solid (80%). Rf 0.37 (hexanes/ethyl acetate 7/3). mp: 117 ºC. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 0.85 (t, J = 6.4 Hz, 3H); 1.24-1.47 (m, 22H); 1.72-1.80 (m, 2H); 4.01 (t, J = 6.8 Hz, 2H); 5.37 (s, 1H); 6.92 (d, J = 8.8 Hz, 2H); 7.07 (m, 4H); 8.10 (d, J = 9.2 Hz, 2H). IR (NaCl, Nujol): 3380, 1725, 1607, 1511, 1465, 1167 cm^{-1}.

Synthesis of 4-(4-n-tetradecyloxy)benzoyloxyphenyl 6-hydroxynicotinate (VIII).

i) Synthesis of 6-benzyloxynicotinic acid. To a solution of sodium hydride (1.90 g, 79.2 mmol) in DMF (80 mL) at 0 ºC was added benzyl alcohol (8.6 mL, 95 mmol). The mixture was stirred at 0 ºC for 20 min and then poured over a cold (0 ºC) solution of 6-chloronicotinic acid in DMF (50 mL). The resulting mixture was heated under reflux for 2 h. After cooling, 100 mL of a solution of acetic acid (5%) were added and the organic material was extracted 3 times with ethyl acetate, washed with brine and evaporated to yield yellow oil. Water was added and the resulting white solid was crystallized from an acetone/water mixture. Yield: 3.20 g of a white solid (88%). Rf 0.48 (hexanes/ethyl acetate 7/3). mp: 171 ºC. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 5.43 (s, 2H); 6.84 (d, J = 8.8 Hz, 1H); 7.30-7.39 (m, 5H); 8.20 (dd, J = 2.4 Hz, J = 8.7 Hz, 1H); 8.92 (d, J = 2.4 Hz, 1H) IR (Nujol, NaCl): 2920 (br), 1735, 1693, 1614, 1460, 1280 cm^{-1}.

ii) Synthesis 4-(4-n-tetradecyloxybenzoyloxy)phenyl 6-benzyloxynicotinate. To a solution of 6 (1.00 g, 2.35 mmol) in distilled dichloromethane (30 mL) were added 6-benzyloxynicotinic acid (0.46 g, 2.35 mmol) and N,N-dimethylaminopyridine (DMAP) (0.029 g, 0.235 mmol) under an argon atmosphere. The mixture was cooled in a water-ice bath and after 30 min, dicyclohexylcarbodiimide (DCC) (0.484 g, 2.35 mmol) was added. The reaction mixture was stirred for 24 h at room temperature. After this time, the white solid was filtered off and the solvent evaporated. The crude product was purified by crystallization from ethyl acetate. Yield: 1.05 g of a white solid (71%). Rf 0.71 (hexanes: ethyl acetate 7:3). Mp: C 100 ºC SmC 121 ºC N 134 ºC I. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 0.88 (t, J = 6.0 Hz, 3H); 1.26-1.51 (m, 22H); 1.80-1.86 (m, 2H); 4.05 (t, J = 6.6 Hz, 2H); 5.50 (s, 2H); 6.89 (d, J = 8.4 Hz, 1H); 6.97 (d, J = 8.8 Hz, 2H); 7.25-7.27 (m, 4H); 7.34-7.49 (m, 5H); 8.14 (d, J = 8.8 Hz, 2H); 8.31 (dd, J = 2.4 Hz, J = 8.8 Hz, 1H); 9.02 (d, J = 2.4 Hz, 1H) IR (Nujol, NaCl): 1734, 1608, 1510, 1480, 1218, 1172 cm$^{-1.}$

iii) Synthesis of 4-(4-n-tetradecyloxy)benzoyloxyphenyl 6-hydroxynicotinate (VIII). $Pd(OH)_2/C$ (20% in weight) (0.200 g) was added over a solution of 4-(4-n-tetradecyloxybenzoyloxy)phenyl 6-benzyloxynicotinate (1.0 g, 1.56 mmol) in THF (50 mL) and cyclohexene (7 mL) under an argon atmosphere. The reaction mixture was heated under reflux for 18 h. After this time, the reaction mixture was allowed to cool down to room temperature and filtered through a pad of Celite®. The solvent was evaporated to yield a white solid, which was crystallized from ethanol. Yield: 0.340 g of a white solid (40%). R_f 0.71 (7/3 hexanes/ethyl acetate). mp: C 148 ºC SmC 230 ºC I. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 0.90 (t, J = 6.3 Hz, 3H); 1.23-1.52 (m, 22H); 1.82-1.86 (m, 2H); 4.07 (t, J = 6.3 Hz, 2H); 6.67 (d, J = 9.6 Hz, 1H); 6.98 (d, J = 8.7 Hz, 2H); 7.28-7.31 (m, 4H); 8.12-8.18 (m, 3H); 8.41 (d, J = 2.1 Hz, 1H); 12.28 (s, 1H). ^{13}C-NMR (300 MHz, $CDCl_3$) δ(ppm): 14.0, 22.7, 26.0, 29.2, 29.3, 29.4, 29.6, 29.7, 31.9, 68.5, 114.5, 122.3, 122.8, 132.3, 140.6, 140.8, 147.9, 148.9, 162.5, 163.5, 164.7. IR (KBr): 1738, 1729, 1608, 1511, 1173 cm^{-1}. MS FAB+ m/z: 317, 548. Anal. for $C_{33}H_{41}NO_6$ (547.67): calcd.: 72.37% C, 7.55% H, 2.56% N, found: 72.50% C, 7.39% H, 2.65% N.

Synthesis of 2-amino-3-(4-(4-n-tetradecyloxybenzoyloxy)phenyliminomethyl)pyridine (IX). To a solution of 4-aminophenyl 4-n-tetradecyloxybenzoate (0.64 g, 1.50 mmol) and 2-amino-3-pyridinecarboxaldehyde (0.19 g, 1.50 mmol) in absolute ethanol (38 mL) were added a few drops of glacial acetic acid. The reaction mixture was heated under reflux for 22 h and allowed to cool to room temperature. A precipitate formed and this was filtered off and washed with ethanol. The solid was purified by crystallization from ethyl acetate. Yield: 0.52 g of a yellow solid (65%). Mp: C 148 ºC N 156 ºC I. ^{1}H-NMR (400 MHz, D8 toluene): δ (ppm): 0.55 (s, < 1H), 0.91-0.93 (m, 3H), 1.25-1.50 (m, 22H), 3.77 (t, 2H, J = 6.4 Hz), 6.35-6.38 (m, 1H), 6.82 (d, 2H, J = 8.7 Hz), 6.88-6.98 (m, broad), 7.10-7.13 (m, 3H), 7.20 (d, 2H, J = 8.6 Hz), 8.05-8.10 (m, 2H), 8.19 (d, 2H, J = 8.7 Hz). IR (KBr): 3340, 3280, 3120, 1720, 1626, 1605, 1558, 1256, 1190, 1161, 1072, 764 cm-1. Anal. for $C_{33}H_{43}O_3N_3$ (529.70): calcd.: 74.82% C, 8.18% H, 7.93% N; found: 74.58% C, 8.17% H, 7.87% N.

Synthesis of 2-amino-3-(4-(4-n-tetradecyloxybenzoyloxy)benzylimino)pyridine (X). To a solution of 4-(4-n-tetradecyloxybenzoyloxy)benzaldehyde (0.44 g, 1.00 mmol) and 2,3-diaminopyridine (0.145 g, 1.33 mmol) in ethanol (20 mL) were added a few drops of glacial acetic acid. The reaction mixture was heated under reflux for 22 h and after this time it was allowed to cool to room temperature. A precipitate formed and this was filtered off, washed with ethanol and then purified by crystallization from ethyl acetate with a few drops of toluene. Yield: 0.234 g of a solid (44%). Mp: C 195 ºC SmC - N 203 ºC I. ^{1}H-NMR (400 MHz, D8 toluene): δ (ppm): 0.27 (s, < 1H), 0.40-0.60 (s, broad, < 1H), 0.91-0.93 (m, 3H), 1.28-1.42 (m, 22H), 1.61-1.72 (m, 2H), 3.78 (t, 2H, J = 6.4), 6.83 (d, 2H, J = 8.7 Hz), 6.91-6.94 (m,1H), 7.29 (d, 2H, J = 8.4 Hz), 7.91 (d, 1H, J = 7.4 Hz), 8.02 (d, 2H, J = 8.0 Hz), 8.19 (d, 2H, J = 8.7 Hz), 8.29-8.31 (m, 1H), 11.5 (s, 1H). IR (KBr): 3050-3200, 2919, 2848, 1732, 1606, 1510, 1470, 1258, 1204, 1165, 1067, 761 cm-1. Anal. for $C_{33}H_{43}O_3N_3$ (529.70): calcd.: 74.82% C, 8.18% H, 7.93% N; found: 74.94% C, 7.85% H, 7.81% N.

Techniques.

NMR experiments were performed on a 400 MHz Bruker Avance spectrometer. Infrared spectra for all the complexes were obtained using a

Mattson Genesis II FTIR spectrophotometer in the 400-4000 cm^{-1} spectral range. Microanalyses were performed with a Perkin-Elmer 2400 microanalyser. Mass spectrometry performed with a VG AutoSpec EBE.

Mesomorphic properties were studied by optical microscopy using an Olympus BH2 microscope with crossed polarizers. The microscope was connected to a Linkam THMS 600 hot stage and an Olympus DP-12 camera. Transition temperatures were determined by differential scanning calorimetry (DSC) using either a TA2910 differential calorimeter or Perkin-Elmer DSC-7 calorimeter. Each apparatus was calibrated with indium (156.6 °C, 28.44 J/g) and tin (232.1 °C, 60.5 J/g) using a scanning rate of 10 °C/min in most cases. X-ray diffraction patterns were obtained with an evacuated Pinhole Camera (Anton-Paar) operating with a point-focused Ni-filtered Cu-$K\alpha$ beam. The samples were held in Lindemann glass capillaries (1 mm diameter) and heated, where necessary, with a variable-temperature attachment. The diffraction patterns were collected on flat photographic film.

Polarization measurements were carried out using commercial cells with ITO electrodes coated with polyimide (LINKAM, 5 μm). The triangular wave voltage was supplied by a HP3325A function generator plus an amplifier and the current was recorded by a HP3458A digital millimetre. All the equipment was interfaced to a microcomputer.

Dielectric permittivity was measured with the HP4192A impedance analyzer using two types of cells, the Linkam cells mentioned above and metallic cells, that consist of two gold-plated electrodes, diameter 5 mm separated by 50 μm thick silica spacers. The cell is located at the end of a coaxial line using as sample holder a modified HP16091A coaxial test fixture. It was held in a cryostat from Novocontrol and both temperature and dielectric measurements were computer controlled.

Table S1. *The spacing (d) corresponding to the low angle reflections obtained from X-ray diffraction studies on the mesophase of some representative H-bonded materials under study, with the Miller indices and the layer parameter (c).*

Complex	**Mesophase assigned**	***d* (Å)**	**Miller indices hkl**	**Parameter (Å)**
V-B14	SmA	49.9	001	c = 49.9
VII-B14	SmC	44.8	001	c = 44.8
VIII-B14	SmC	42.0	001	c = 42.0
X-B14	SmCP	41.9 20.6 13.7	001 002 003	c = 41.4
V	SmA	38.4	001	c = 38.4
VIII	SmC	46.2	001	c = 46.2
B14	SmC	35.0	001	c = 35.0

Figure S1. *Schematic representations used for bent-shaped molecules (upper part); models proposed for the arrangements of the molecules in the columnar mesophase and models proposed for some of the arrangements in the SmCP packing (B_2), which are distinguished by the relative tilt sense and the polar order in the smectic layers. S and A denote sinclinic or an anticlinic tilt and F and A behind P refer to a ferro- or antiferroelectricelectric polar order.*

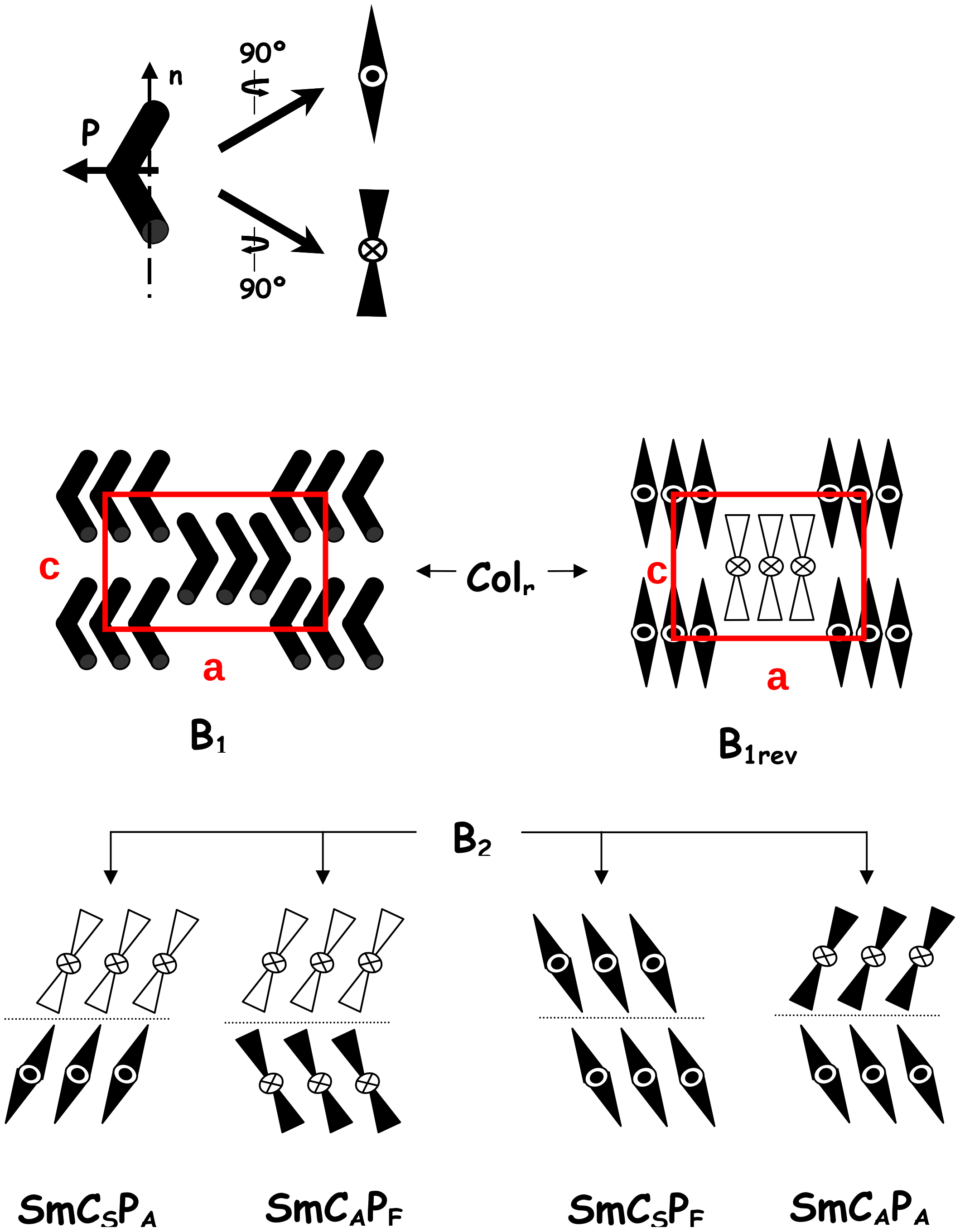


Figure S2. *IR spectra of compounds* ***VIII*** *at variable temperature: solid at r.t. (red), at 140 ºC in the SmC mesophase (green) and at r.t. after thermal treatmet (blue) in KBr.*

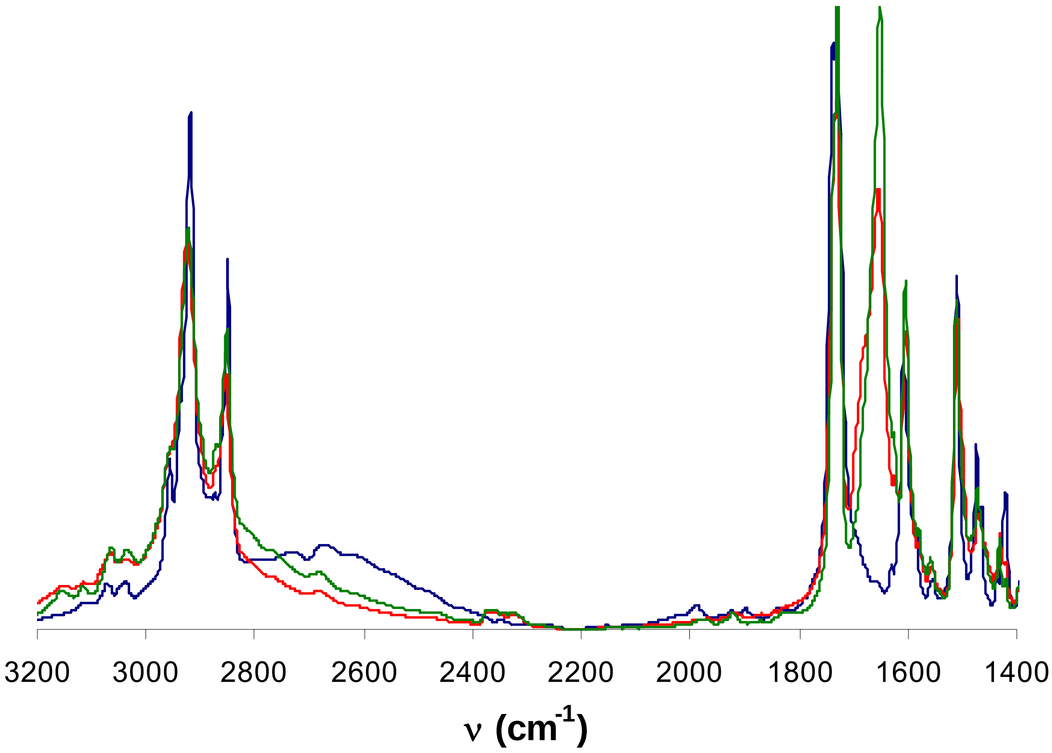
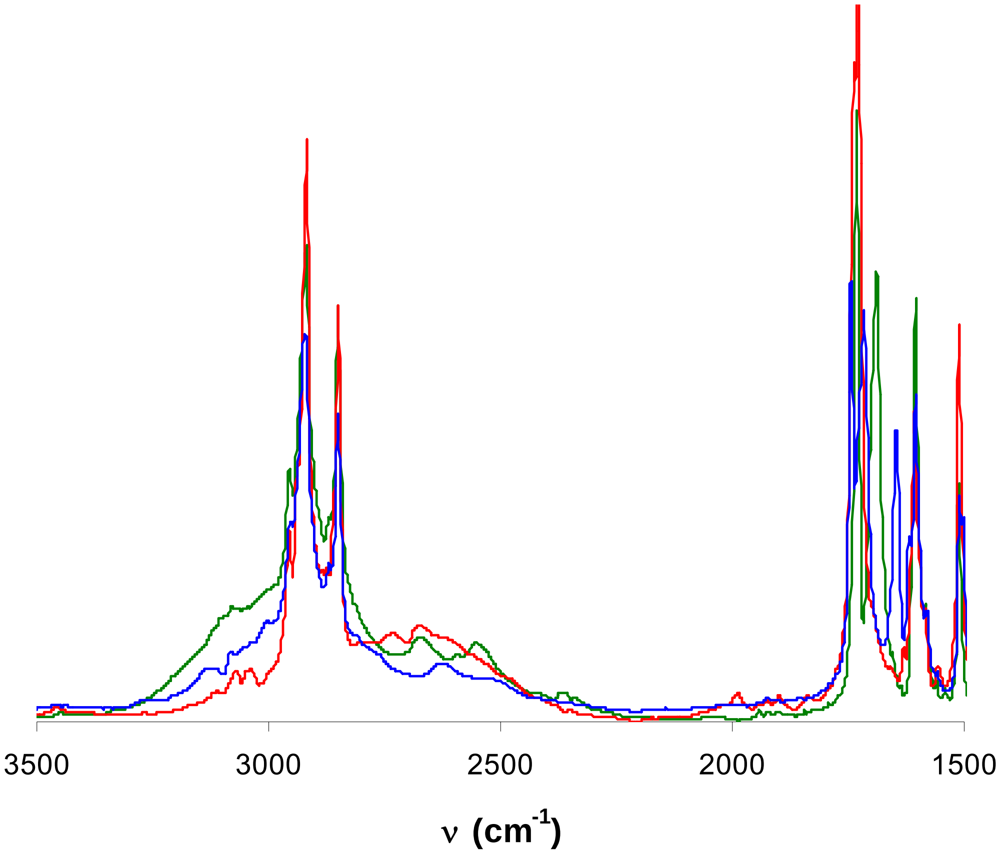


Figure S3. *IR spectra of compounds* ***VIII*** *(red),* ***B14*** *(green) and the blend of both [****VIII-B14****]: at room temperature (bold blue) and in the SmC mesophase at 150 ºC (dashed blue) in KBr.*



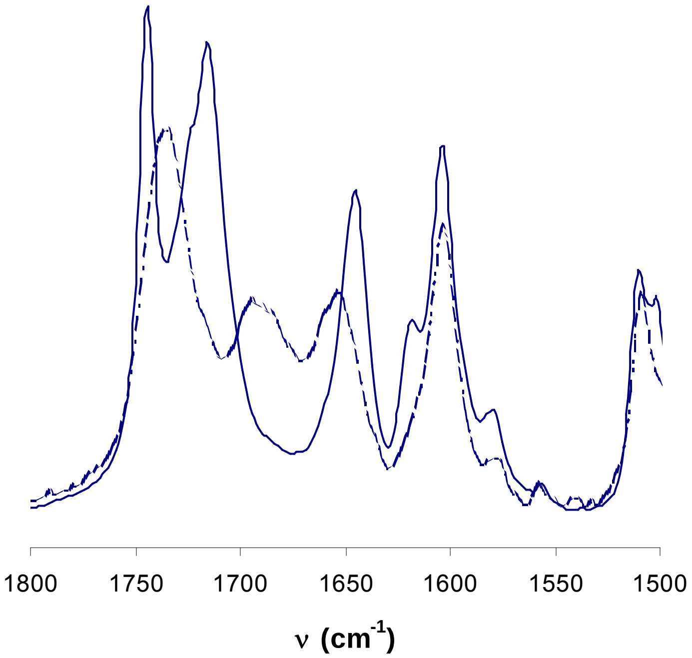


Figure S4. *IR spectra of compounds* ***VII*** *(red),* ***B14*** *(green) and* ***VII-B14*** *at room temperature, in the nematic and in the SmC mesophase (different blues) in KBr.*

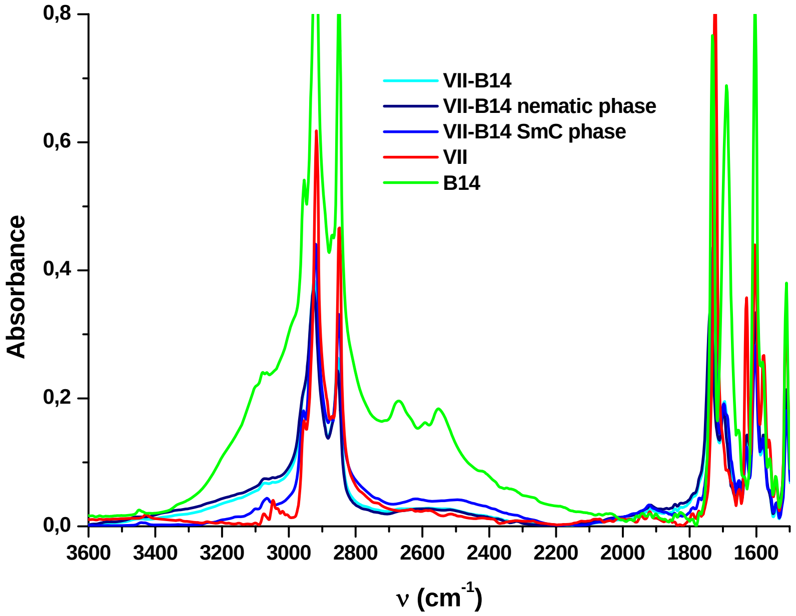


Figure S5. *IR spectra of compounds* ***X*** *(red),* ***B14*** *(green) and the blend of both [****X+B14****] (blue) at room temperature in KBr.*