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Formation of hexagonal columnar phases by heterocyclic pyrimidine derivatives

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The synthesis, characterization, and mesomorphic properties of a new type of heteronuclear compounds derived from pyrimidine as core group are reported. These compounds were prepared by condensation reactions of appropriate acetophenones and benzonitriles in the presence of trifluoromethanesulphonic anhydride. They were characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis, and their phase transitions characterized and studied by thermal analysis and polarizating microscopy. These compounds exhibit hexagonal columnar (Col_h) phases, as expected for disk-like molecules; the formation of columnar phases was found to be dependent on the numbers of alkoxy side chains attached. For those compounds having the same numbers of flexible side chains attached, the one with a preferred unsymmetric structure exhibited better mesomorphic properties. The observed improved mesomorphic behaviour of these compounds over other similar all-carbon heterocyclic compounds is attributed to the greater polarization of nitrogen atoms in the core ring.

1. Introduction

Numerous new mesogenic compounds exhibiting columnar phases have been prepared and studied since the discovery of the first thermotropic discotic liquid crystals by Chandrasekhar *et al.* [1] in 1977. A better understanding of the relationship between molecular structure and mesomorphic properties will assist in the development of materials for advanced applications. In general, molecular structures with an overall circular geometric shape are crucially required for formation of columnar phases. However, rod-like molecules are also known to generate such columnar phases in an anti-parallel arrangement [2]. The formation of columnar phases is also found to be dependent on side chain density around the central core group. On the other hand, adding more side chains and/or extending longer carbon chains are essential for disc-shaped molecules with a larger or more rigid core group. Typical phases observed in these discotic materials are hexagonal columnar (Col_h), rectangular columnar (Col_r) and nematic discotic phases (N_D).

Numerous examples of hydrocarbon structures [3] used as core groups exhibiting columnar phases have been reported. However, examples of heterocyclic structures [4, 5] used as core groups are relatively fewer. The presence of nitrogen, sulfur or oxygen atoms in these heterocyclic rings [4, 5], which probably introduce a transverse dipole moment, often result in a change in dielectric anisotropy. The formation of liquid crystallinity in such heterocyclic compounds might be facilitated by weak π–π interaction between these aromatic or heterocyclic rings.

In this work, a new type of disc-like compounds **1–7** in which an unsaturated pyrimidine ring is utilized as the rigid core group, were prepared and their mesomorphic properties studied (see the figure). Compounds **3–7** exhibited columnar phases; compounds **1**,**2** were non-mesogenic.

2. Results and discussion

2.1. *Synthesis and characterization*

Typical synthetic pathways to the pyrimidine derivatives (compounds **1**,**2** or **5–7**) are summarized in schemes 1 and 2. Original attempts to prepare these compounds by condensation [6] or β-diketones and benzaldehydes in the presence of sodium hydride and ammonium acetate with bubbling oxygen were unsuccessful. Instead, these compounds were obtained by the condensation of appropriate substituted acetophenones with two equivalents of benzonitriles and trifluoromethanesulphonic anhydride in dried nitroethane [7]. The reaction products isolated varied with the numbers of alkoxy side chains in the

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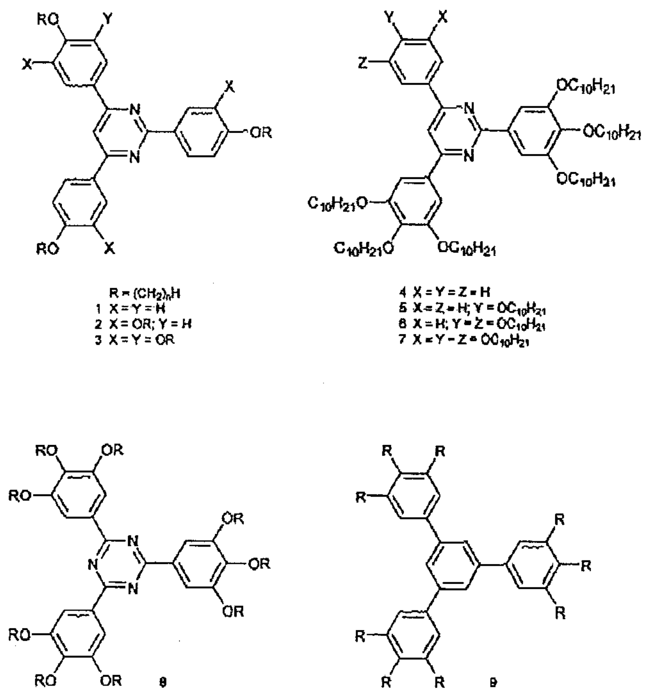
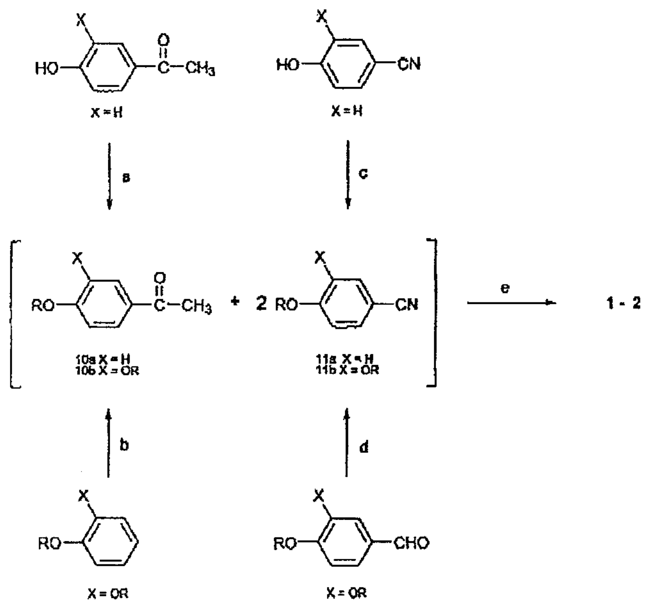
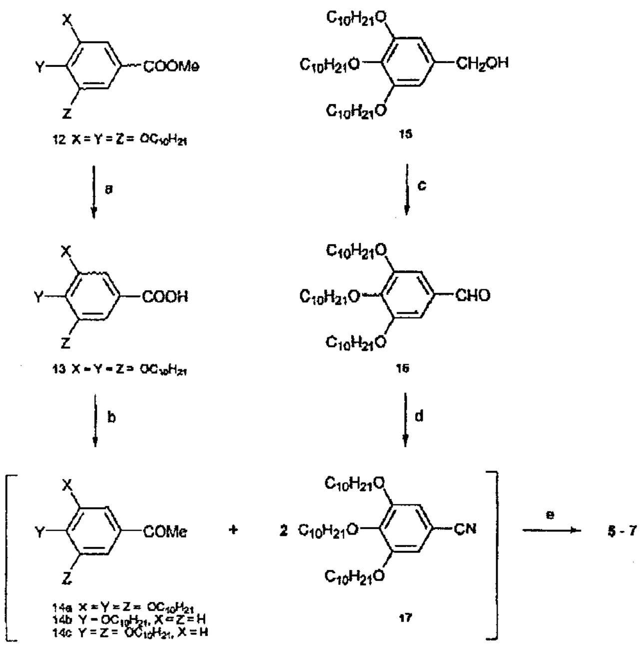


Figure. Structures of the compounds studied.



Scheme 1. Conditions and reagents: (a) *n*-alkyl bromide (1.0 eq), K_2CO_3 (2.0 eq), reflux in CH_3COCH_3, 24 h, 71–92%; (b) CH_3COCl (1.1 eq), stirred at rt, then reflux in CH_2Cl_2, 12 h, 71–83%; (c) *n*-alkyl bromide (1.0 eq), K_2CO_3 (2.0 eq), reflux in DMF, 24 h, 69–78%; (d) pyridine hydrochloride (1.5 eq), reflux in nitroethane, 12 h, 79–87%; (e) trifluoromethane sulphonic anhydride (1.0 eq), stirred at rt, in CH_2Cl_2, 48 h.

reactants used. Reactions of 4-alkoxyacetophene **10a** or 3,4-dialkoxyacetophenone **10b** and 4-alkoxybenzonitrile **11a** or 3,4-dialkoxybenzonitrile **11b** as reactants



Scheme 2. Conditions and reagents: (a) KOH (3.0 eq), reflux in THF/H_2O (9/1), 24 h, 82–96%; (b) methyl lithium (2.0 eq), stirred at rt, then reflux in dried THF, 12 h, 72–84%; (c) pyridinium chlorochromate (2.0 eq), stirred at rt in CH_2Cl_2, 3 h, 75–85%; (d) pyridine hydrochloride (1.5 eq), reflux in nitroethane, 12 h, 81–89%; (e) trifluoromethane sulphonic anhydride (1.1 eq), stirred in CH_2Cl_2, at rt, 48 h.

gave only the single products 2,4,6-tri(4′-alkoxyphenyl)pyrimidine **1** or 2,4,6-tri(3′,4′-dialkoxyphenyl)pyrimidine **2**. However, when a tri-substituted reactant; 3,4,5-trialkoxyacetophene **14a–c** and/or 3,4,5-trialkoxybenzonitrile **17** were used, this reaction gave a mixture of two products: 2,4,6-tri(3′,4′,5′-trialkoxyphenyl)pyrimidine **3–7** and 2,4,6-tri(3′,4′5′-trialkoxyphenyl)-1,3,5-triazine **8**. These products were separated and purified by flash chromatography; the yields of compounds **3–7** and **8** were in the range 19–32% and 39–53%, respectively. All these reported compounds were characterized by ^1H and ^{13}C NMR, mass spectroscopy and elemental analysis. Toward the close of our work, a series of 2,4,6-tri(3,4,5-trialkoxyphenyl)triazines was reported [8]; these compounds were prepared by the reaction of 3,4,5-trialkoxybenzonitriles in trifluoromethanesulphonic anhydride. Therefore this series of triazine derivatives, although found to exhibit hexagonal columnar phases, is excluded from this paper.

2.2. *Mesomorphic properties*

A few disc-like all-carbon compounds [9] based on hexa- and nona-substituted 1,3,5-triphenylbenzenes **9** were previously prepared by Scherowsky. These all-carbon benzene-based derivatives with chiral or non-chiral ester substituents were found to be non-mesogenic.

The lack of mesomorphic properties observed in this type of disc-like molecule was attributed to the absence of delocalization of π-electrons over all four rings due to non-planar conformations. However, some derivatives used as dopants did induce cholesteric phases in nematic discotics. In this work a series of structurally similar compounds in which two of the carbon atoms on the central benzene core group are replaced by two N atoms were prepared, and their mesomorphic properties studied. The presence of two nitrogen atoms in this heterocyclic ring might produce a change in dielectric anisotropy, and possibly induce mesomorphic behaviour.

The liquid crystalline behaviour of compounds **1–7** was studied by thermal analysis (DSC) and polarizing optical microscopy. The phase transitions and thermodynamic data are summarized in the table. The formation of columnar mesophases was found to be dependent on the number of flexible side chains attached to the core group. All compounds of type **1**,**2** formed crystalline phases regardless of the carbon length of the alkoxy side chains. The lack of liquid crystallinity in compounds **1** and **2** with three or six side chains, respectively, was supposed due to an insufficiency of side chain density for formation of a stable columnar phase. The formation of columnar phases was generally found to depend crucially on the side chain density, and most columnar mesogens have at least six side chains. In fact a few examples of metallomesogenic structures with three side chains which exhibit columnar phases have been reported [10]. The molecules in this type of correlated columnar phase are generally organized with an antiparallel arrangement within the columns.

Table. Phase behaviour of compounds **1–7**: *n* represents the number of carbons in the alkoxy chain. Cr = crystal; Col_{hd} = disordered hexagonal columnar; I = isotropic. The transition temperature (°C) and enthalpies (in parentheses, kJ mol^{-1}) determined by DSC at a scan rate of 10.0°C min^{-1}.

Compound	*n*	Transitions
1	8	$Cr \underset{31.5\ (28.7)}{\overset{74.8\ (32.6)}{\rightleftharpoons}} I$
	12	$Cr \underset{33.8\ (57.8)}{\overset{64.5\ (48.7)}{\rightleftharpoons}} I$
2	8	$Cr \underset{80.0\ (50.9)}{\overset{101.3\ (47.5)}{\rightleftharpoons}} I$
	12	$Cr \underset{83.5\ (89.6)}{\overset{106.7\ (83.1)}{\rightleftharpoons}} I$
3	10	$Cr \underset{34.6\ (34.9)}{\overset{59.7\ (32.5)}{\rightleftharpoons}} Col_{hd} \underset{97.7\ (3.85)}{\overset{105.0\ (4.96)}{\rightleftharpoons}} I$
4	10	$Cr \underset{37.9\ (34.2)}{\overset{45.7\ (36.0)}{\rightleftharpoons}} Col_{hd} \underset{73.6\ (2.57)}{\overset{82.9\ (2.70)}{\rightleftharpoons}} I$
5	10	$Cr \underset{41.5\ (48.5)}{\overset{56.5\ (49.0)}{\rightleftharpoons}} Col_{hd} \underset{104.0\ (3.20)}{\overset{114.0\ (3.70)}{\rightleftharpoons}} I$
6	10	$Cr \underset{5.92\ (27.0)}{\overset{36.2\ (26.6)}{\rightleftharpoons}} Col_{hd} \underset{124.3\ (5.35)}{\overset{131.4\ (5.03)}{\rightleftharpoons}} I$
7	10	$Cr \underset{34.0\ (15.0)}{\overset{62.1\ (15.6)}{\rightleftharpoons}} Col_{hd} \underset{134.4\ (6.23)}{\overset{140.5\ (6.52)}{\rightleftharpoons}} I$

However, all the compounds **3–7** with enhanced side chains exhibited columnar phases. Interestingly, compound **4**, which has six side chains, the same as compound **2**, formed a columnar phase. The better mesomorphic properties for compound **4** over **2** is attributed to an unsymmetric structure, which results in a less regular packing in the solid states. Continuing to increase the numbers of side chains from seven (**5**), eight (**6**) to nine (**7**) resulted in improved mesomorphic behaviour. Thermal results showed that compounds **3–7** exhibit enantiotropic behaviour. In DSC all the compounds melt to give crystal-to-columnar and columnar-to-isotropic transitions (Cr → Col → I), typical for discotic molecules. Mesophase-to-isotropic transitions for the compounds were observed in the lower temperature range at 36.2–140.5°C on heating, and the temperature range of the columnar phase was 36–119°C. This temperature range increased with the numbers of side chains, with compounds **6** and **7** having a wider temperature range than other compounds. The mesophase was characteristically identified as hexagonal columnar (Col_h) based on optical texture observations. A typically pseudo focal-conic texture with linear birefringent defects was clearly observed on slow cooling from the isotropic liquid, as often obtained for discotic molecules. In addition, a relatively smaller enthalpy for the columnar-to-isotropic transition was observed indicating that the mesophases were highly disordered.

3. Summary

A new class of disc-like heterocyclic molecules based on pyrimidine derivatives as core group has been prepared, and these compounds have been demonstrated to exhibit columnar phases. The presence of nitrogen atoms, which are more polarized, in the heterocyclic ring believed to be responsible for the enhanced mesomorphic properties over other analogous all-carbons rings. In addition molecules with a lower symmetry or unsymmetrical structure are readily amenable to the formation of columnar phases.

4. Experimental

All chemicals and solvents were reagent grades from Aldrich Chemical Co. ^{1}H and ^{13}C NMR spectra were measured on a Bruker DRS-200 instrument. DSC thermographs were carried out on a Mettler DSC-820 calibrated with pure indium. All phase behaviour was determined at a scan rate of 10.0°C min^{-1}. Polarizating microscopy was carried out on Nikkon MICROPHOT-FXA with a Mettler FP-90/FP82HT hot stage system. Elemental analysis for carbon, hydrogen, and nitrogen was conducted on a Heraeus CHN-O-Rapid elemental analyser. The compounds 4-alkoxyacetophenones [11 *a*], 3,4-dialkoxy acetophenones [11 *b*], 3,4-dialkoxybenzaldehydes [11 *c*], 3,4,5-trialkoxy benzoic acids [11 *a*] 3,4,5-trialkoxyacetophenones [11 *a*], 3,4,5-trialkoxybenzoylalcohols [11 *c*] and 3,4,5-trialkoxybenzaldehydes [11 *c*] were prepared by literature methods.

4.1. *4-Dodecyloxyacetophenone (**10a**, n = 12)*

White crystals, yield 86%, m.p. 48–49°C. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, $-CH_3$, 3H), 1.24–1.81 (m, $-CH_2$, 16H), 2.52 (s, $-COCH_3$, 3H), 3.98 (t, $-OCH_2$, 2H), 6.87 (d, −Ar, 2H), 7.88 (d, −Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 13.88, 15.49, 23.26, 26.95, 27.31, 29.67, 29.93, 30.21, 32.50, 68.78, 113.50, 115.85, 129.60, 129.70, 130.64, 163.38, 196.36. IR (KBr): 2960, 2873, 1678 (CO), 1600, 1507, 1254, 1111 cm^{-1}.

4.2. *4-Dodecyloxybenzonitrile (**11a**, n = 12)*

White crystals, yield 87%, m.p. 42–43°C. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, $-CH_3$, 3H), 1.24–1.80 (m, $-CH_2$, 20H), 3.96 (t, $-OCH_2$, 2H), 6.86 (d, −Ar, 2H), 7.52 (d, −Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 13.76, 13.82, 22.42, 25.67, 28.72, 29.09, 29.32, 29.39, 31.67, 68.14, 103.38, 114.90, 118.89, 133.55, 162.20. IR (KBr): 2919, 2859, 2223 (CN), 1613, 1513, 1261, 1182, 844, 552 cm^{-1}.

4.3. *3,4-Didodecyloxyacetophenone (**10b**, n = 12)*

White crystals, yield 75%, m.p. 60–62°C. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, $-CH_3$, 6H), 1.23–1.81 (m, $-CH_2$, 40H), 2.52 (s, $-CH_3$, 3H), 4.03 (t, $-OCH_2$, 4H), 6.86 (d, −Ar, 1H), 7.49 (s, −Ar, 1H), 7.53 (d, −Ar, 1H). ^{13}C NMR ($CDCl_3$): δ 14.06, 14.11, 15.44, 22.64, 25.94, 26.14, 29.00, 29.12, 29.33, 29.58, 30.13, 31.88, 32.54, 68.97, 69.17, 111.48, 112.30, 123.12, 130.20, 148.78, 153.47, 196.82. IR (KBr): 2939, 2866, 1676 (CO), 1593, 1520, 1434, 1281, 1215, 1149, 1082, 804, 651 cm^{-1}.

4.4. *3,4-Didodecyloxybenzaldehyde*

White crystals, yield 69%. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, $J = 5.46$ Hz, $-CH_3$, 6H), 1.23–1.81 (m, $-CH_2$, 40H), 4.05 (t, $J = 4.38$ Hz, $-OCH_2$, 4H), 6.92 (d, −Ar, $J = 7.74$ Hz, 1H), 7.36 (s, −Ar, 1H), 7.41 (d, −Ar, $J = 1.99$ Hz, 1H), 9.80 (s, −CHO, 1H). ^{13}C NMR ($CDCl_3$): δ 14.03, 22.31, 22.63, 25.30, 25.94, 28.98, 29.06, 29.31, 29.57, 31.21, 31.88, 68.92, 69.10, 111.03, 111.92, 126.54, 130.16, 149.81, 154.83, 190.27. IR (KBr): 29.32, 2853, 1699 (CO), 1600, 1520, 1467, 1434, 1393, 1281, 1241, 1149, 811 cm^{-1}.

4.5. *3,4-Didecyloxybenzonitrile (**11b**, n = 12)*

Light yellow crystals, yield 69%, m.p. 81–83°C. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, $-CH_3$, 6H), 1.24–1.81 (m, $-CH_2$, 40H), 3.98 (t, $-OCH_2$, 4H), 6.85 (d, −Ar, 1H), 7.04 (s, −Ar, 1H), 7.21 (d, −Ar, 1H). ^{13}C NMR ($CDCl_3$): δ 13.80, 22.42, 23.05, 24.87, 25.70, 28.62, 28.72, 29.02, 29.06, 30.55, 31.54, 31.56, 68.58, 69.10, 103.36, 112.54, 115.46, 125.60, 148.62, 152.72, 119.07. IR (KBr): 2932, 2853, 2229 (CN), 1600, 1513, 1467, 1281, 1241, 1142, 996, 804 cm^{-1}.

4.6. *3,4,5-Tridecyloxybenzoic acid (**13**, n = 10)*

White crystals, yield 75%. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, $J = 4.30$ Hz, $-CH_3$, 9H), 1.18–1.84 (m, $-CH_2$, 48H), 3.99 (m, $-OCH_2$, 6H), 7.33 (s, −Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 14.09, 22.68, 26.05, 29.61, 30.30, 31.91, 69.07, 73.49, 108.39, 123.66, 143.00, 152.77, 172.21 (CO). IR (KBr): 3460 (OH), 2936, 2848, 1685 (CO), 1590, 1471, 1435, 1335, 1219, 1119, 970 cm^{-1}.

4.7. *3,4,5-Tridecyloxyacetophenone (**14a**, n = 10)*

White crystals, yield 78%, m.p. 37–38°C. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $J = 4.30$ Hz, $-CH_3$, 9H), 1.24–1.84 (m, $-CH_2$, 48H), 2.53 (s, $COCH_3$, 3H), 3.97–4.03 (m, $-OCH_2$, 6H), 7.15 (s, −Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 13.98, 22.55, 26.28, 29.21, 30.21, 31.49, 31.64, 25.67, 69.25, 73.44, 107.14, 132.04, 142.88, 152.85, 196.98 (CO). IR (KBr): 2925, 2854, 1679 (CO), 1585, 1472, 1434, 1333, 1122, 724 cm^{-1}.

4.8. *3,4,5-Tridecyloxybenzylalcohol (**15**, n = 10)*

White solid, yield 90%, m.p. 44–45°C. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, $J = 4.90$ Hz, $-CH_3$, 9H), 1.24–1.80 (m, $-CH_2$, 48H), 3.94 (m, $-OCH_2$, 6H), 4.59 (s, $-CH_2OH$, 2H), 6.51 (s, −Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 14.09, 22.67, 26.13, 29.40, 29.68, 29.75, 31.98, 62.25, 68.85, 73.25, 115.0, 136.0, 137.6, 153.0. IR (KBr): 3323 (OH), 2952, 2872, 1593, 1507, 1440, 1341, 1235, 1116, 830, 704 cm^{-1}.

4.9. *3,4,5-Tridecyloxybenzaldehyde (**16**, n = 10)*

Light yellow paste, yield 79%. ^{1}H NMR ($CDCl_3$): δ 0.89 (t, $J = 4.70$ Hz, $-CH_3$, 9H), 1.30–1.85 (m, $-CH_2$, 48H), 4.02 (m, $-OCH_2$, 6H), 7.02 (s, −Ar, 2H), 9.80 (s, −CHO, 1H). ^{13}C NMR ($CDCl_3$): δ 14.10, 22.60, 26.34, 29.23, 29.67, 30.32, 31.91, 69.30, 73.62, 108.78, 123.76, 143.37, 152.92, 191.04 (CHO). IR (KBr): 2920, 2840, 1690, 1580, 1490, 1460, 1440, 1370, 1320, 1220, 1110, 740 cm^{-1}.

4.10. *3,4,5-Tridecyloxybenzonitrile (**17**, n = 10)*

A mixture of 3,4,5-tridecyloxybenzaldehyde (5.00 g, 8.76 mmol) and pyridine hydrochloride (1.52 g, 13.1 mmol) was heated under gentle reflux in dried nitroethane (100 ml) for 12 h. The reaction was monitored by TLC.

Methylene chloride (100 ml) was added to the solution, and the reaction mixture was then extracted with 100 ml dilute hydrochloric acid (0.1M). The collected organic layers were washed three times with water. The organic layers were combined and dried with anhydrous $MgSO_4$, then concentrated to give a crude yellow oil. The final product was isolated as a yellow solid by recrystallization from methylene chloride/methanol (1/3), or by silica gel chromatography eluting with hexane/ethyl acetate (40/1). Light yellow solid, yield 77%, m.p. 50.6–52.0°C. ^{1}H NMR ($CDCl_3$), δ 0.85 (t, $J=4.90$ Hz, $-CH_3$, 9H), 1.24–1.85 (m, $-CH_2$, 48H), 3.91–4.00 (m, $-OCH_2$, 6H), 6.78 (s, −Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 13.81, 22.50, 25.85, 29.03, 29.18, 29.35, 29.40, 29.43, 29.43, 29.55, 30.13, 31.74, 69.14, 73.37, 106.09, 110.21, 118.84 (CN), 141.25, 153.25. IR (KBr): 2923, 2866, 2236 (CN), 1586, 1507, 1474, 1434, 1248, 1135, 844, 625 cm^{-1}.

4.11. *2,4,6-Tri(3′,4′-didodecyloxyphenyl)pyrimidine (**2**, n = 12)*

A mixture of 3,4-didodecyloxybenzonitrile (4.95 g, 10.5 mmol) dissolved in dried methylene chloride (30 ml and trifluoromethanesulphonic anhydride (1.61 g, 5.70 mmol) was prepared under nitrogen. 3,4-Didodecyloxyacetophenone (2.44 g, 5.00 mmol) dissolved in dried methylene chloride (75 ml) was added dropwise during 1 h. The solution turned reddish, and was stirred for 48 h at room temperature. The solution was extracted with saturated sodium bicarbonate (50 ml), and the organic layer was collected and dried over anhydrous $MgSO_4$. This solution was concentrated to give a black paste which was purified by flash chromatography eluting with hexane/ethyl acetate (40/1). The product was obtained as light yellow crystals after recrystallization from methylene chloride/methanol (1/3). Yield 26%, m.p. 106–108°C. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $J=4.20$ Hz, $-CH_3$, 18H), 1.25–1.87 (m, $-CH_2$, 120H), 4.07–4.16 (m, $-OCH_2$, 12H), 6.98 (d, $J=8.50$ Hz, −Ar, 3H), 7.74–7.77 (d, $J=600$ Hz, 2H), 7.77 (s, 1H), 7.88 (d, $J=7.50$ Hz, 2H), 8.25 (s, −Ar, 1H), 8.25–8.28 (d, $J=7.60$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 14.06, 22.63, 26.02, 26.09, 26.11, 29.25, 29.28, 29.35, 29.43, 29.70, 29.88, 31.66, 31.82, 69.10, 69.45, 108.20, 112.75, 113.03, 113.62, 120.37, 121.75, 130.30, 131.04, 148.75, 149.22, 151.43, 151.60, 163.83. FAB-MS (*m*/*z*) 1414.3 (MH^+, 100%). IR (KBr): 2956, 2854, 1605, 1576, 1517, 1464, 1394, 1374, 1273, 1224, 1121, 800, 722 cm^{-1}. Anal: calcd for $C_{94}H_{160}N_2O_6$, C 79.83, H 11.40, N 1.98; found, C 79.54, H 11.17, N 1.93%.

4.12. *2,4,6-Tri(4′-dodecyloxyphenyl)pyrimidine (**4**, n = 12)*

White crystals, yield 51%, m.p. 64.0–66.0°C. ^{1}H NMR ($CDCl_3$): δ 0.92 (t, $J=4.38$ Hz, $-CH_3$, 9H), 1.21–1.90 (m, $-CH_2$, 60H), 3.93–4.02 (m, $-OCH_2$, 6H), 6.09–7.04 (m, −Ar, 6H), 7.74 (s, Ar, 1H), 8.20 (d, $J=8.40$ Hz, ArH, 4H), 8.68 (d, $J=8.50$ Hz, ArH, 2H). ^{13}C NMR ($CDCl_3$): δ 14.09, 22.68, 26.03, 29.22, 29.28, 29.34, 29.40, 29.58, 29.63, 30.11, 31.90, 68.08, 68.18, 107.82, 114.20, 114.68, 128.74, 129.78, 130.07, 130.61, 161.36, 161.41, 163.76, 163.80. HRMS (FAB): calcd. for MH^+ $C_{58}H_{88}N_2O_3$ 861.6874, found 861.6898. IR (KBr): 2926, 2857, 1608, 1587, 1568, 1529, 1512, 1419, 1368, 1255, 1176, 1042, 825, 783, 523 cm^{-1}. Anal: calcd for $C_{58}H_{88}N_2O_7$, C 80.88, H 10.30, N 3.25; found, C 80.60, H 10.29, N 3.02%.

4.13. *2,4-Bis(3′,4′-didecyloxyphenyl)-6-(3′,4′,5′-tridecyloxyphenyl)pyrimidine (**3**, n = 10)*

Light yellow solid, yield 14%. m.p. 105°C. ^{1}H NMR ($CDCl_3$): δ 0.83 (t, $-CH_3$, 21H), 1.24–1.91 (m, $-CH_2$, 112H), 4.01–4.16 (m, $-OCH_2$, 14H), 6.98 (d, 1H), 7.43 (s, 2H), 7.73 (s + d, 2H), 7.89 (s, pyrimidine−H, 1H), 8.24 (s + d, 2H). ^{13}C NMR ($CDCl_3$): δ 14.08, 22.66, 26.03, 26.14, 29.36, 29.60, 30.36, 31.90, 69.17, 69.56, 73.59, 106.23, 108.66, 113.01, 113.70, 118.66, 120.06, 121.75, 130.39, 131.33, 132.85, 140.06, 148.83, 149.30, 151.49, 151.73, 153.44, 164.13. FAB-MS (*m*/*z*); calcd 1402.19, found 1402.3 IR (KBr): 2926, 2853, 1573, 1520, 1474, 1361, 1269, 1116, 844, 753, 778 cm^{-1}. Anal: calcd for $C_{92}H_{156}N_2O_7$, C 78.80, H 11.21, N 2.00; found, C 78.54, H 10.96, N 2.26%.

4.14. *2,4-Bis(3′,4′,5′-tridecyloxyphenyl)-6-phenylpyrimidine (**4**, n = 10)*

Off white solid, yield 10%, m.p. 83.0°C. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, $-CH_3$, 18H), 1.25–1.89 (m, $-CH_2$, 96H), 4.02–4.15 (m, $-OCH_2$, 12H), 7.45 (s, −Ar, 2H), 7.55 (t, −Ar, 3H), 7.84 (s, pyrimidine−H, 1H), 7.93 (s, 2H), 8.21–8.24 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 14.01, 22.63, 26.14, 29.34, 29.48, 29.60, 30.36, 31.88, 68.94, 69.16, 73.38, 105.83, 106.93, 109.24, 127.14, 128.69, 130.47, 132.24, 132.99, 137.62, 140.67, 140.86, 152.98, 153.34, 163.84, 163.96, 164.35. FAB-MS (*m*/*z*): calcd 1246.04, found 1246.1. IR (KBr): 2926, 2860, 1573, 1540, 1467, 1368, 1229, 1123, 851 cm^{-1}. Anal: calcd for $C_{82}H_{136}N_2O_6$, C 79.05, H 11.00, N 2.25; found, C 78.91, H 10.97, N 2.19%.

4.15. *2,4-Bis(3′,4′,5′-tridecyloxyphenyl)-6-(4′-decyloxyphenyl)pyrimidine (**5**, n = 10)*

Off white solid, yield 11%, m.p. 114.0°C. ^{1}H NMR ($CDCl_3$): δ 0.86 (t, $-CH_3$, 21H), 1.25–1.88 (m, $-CH_2$, 112H), 4.00–4.16 (m, $-OCH_2$, 14H), 7.01–7.06 (d, −Ar, 2H), 7.46 (s, −Ar, 2H), 7.77 (s, pyrimidine−H, 1H), 7.92 (s, 2H), 8.17–8.22 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 14.08, 22.67, 26.03, 26.20, 29.21, 29.38, 29.51, 29.61, 29.67, 30.37, 31.91, 68.21, 69.11, 69.34, 73.48, 73.50, 106.04, 107.07, 108.69, 114.75, 128.69, 129.80, 132.63, 133.25, 140.70, 140.84, 153.07, 153.43, 161.48, 163.98, 164.07. FAB-MS (*m*/*z*): calcd 1402.19, found 1402.3. IR (KBr): 2926, 2853, 1573, 1534, 1501, 1474, 1361, 1116, 771 cm^{-1}. Anal: calcd for $C_{92}H_{156}N_2O_7$, C 78.80, H 11.21, N 2.00; found, C 78.51, H 11.29, N 1.83%.

4.16. *2,4-Bis(3′,4′,5′-tridecyloxyphenyl)-6-(3′,4′-didecyloxyphenyl)pyrimidine (**6**, n = 10)*

Light yellow solid, yield 12%, m.p. 131.4°C. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, $-CH_3$, 24H), 1.49–1.89 (m, $-CH_2$, 128H), 4.01–4.15 (m, $-OCH_2$, 16H), 7.00 (s, 2H), 7.45 (s, 2H), 7.76 (s, 1H), 7.90–7.92 (s + d, 3H). ^{13}C NMR ($CDCl_3$): δ 14.08, 22.69, 26.03, 26.13, 26.17, 29.21, 29.38, 29.50, 29.63, 29.75, 30.36, 31.91, 69.00, 69.18, 69.38, 69.47, 73.50, 73.60, 106.13, 106.92, 108.85, 112.87, 113.14, 120.36, 130.24, 132.64, 133.15, 140.64, 140.89, 149.28, 151.74, 153.04, 153.44, 163.77, 164.05. FAB-MS (*m*/*z*): calcd 1558.34, found 1558.0. IR (KBr): 2926, 2853, 1573, 1507, 1474, 1361, 1116, 874, 753 cm^{-1}. Anal: calcd for $C_{102}H_{176}N_2O_8$, C 78.61, H 11.38, N 1.80; found C 78.42, H 11.02, N 1.62%.

4.17. *2,4,6-Tri(3′,4′,5′-tridecyloxyphenyl)pyrimidine (7, n = 10)*

Reddish-brown solid, yield 13%, m.p. 140.5°C. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, $J = 4.40$ Hz, $-CH_3$, 27H), 1.25–1.86 (m, $-CH_2$, 144H), 4.01–4.12 (m, $-OCH_2$, 18H), 7.44 (s, 4H), 7.72 (s, 1H), 7.92 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 14.06, 22.66, 26.14, 29.36, 29.48, 29.61, 29.66, 30.36, 31.91, 68.99, 69.51, 73.51, 73.63, 106.37, 106.93, 109.41, 132.60, 133.00, 140.70, 141.06, 153.05, 153.46, 163.78, 164.32. FAB-MS (*m*/*z*): calcd 1714.49, found 1714.59. IR (KBr): 2926, 2860, 1573, 1534, 1501, 1361, 1229, 1116, 862, 750 cm^{-1}. Anal: calcd for $C_{112}H_{196}N_2O_9$, C 78.45, H 11.52, N 1.63; found C 78.52, H 11.41, N 1.74%.

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