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Designing banana-shaped liquid crystals without Schiff's base units: *m*-terphenyls, 2,6-diphenylpyridines and V-shaped tolane derivatives

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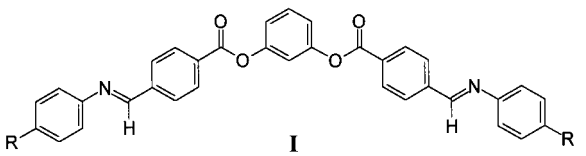
This paper reports attempts to obtain (anti)ferroelectric switchable achiral banana-shaped molecules without Schiff's base units. For this purpose we have synthesized novel V-shaped molecules consisting of rigid angular central units [1,3-disubstituted benzene, 2,7-disubstituted naphthalene, 1,3-diphenylbenzene, 2,6-diphenylnitrobenzene, 2,6-diphenylpyridine, 1,3-bis(phenylethynyl)benzene, 1-phenyl-3-(phenylethynyl)benzene] connected *via* ester linkages to two rigid cores (1,4-disubstituted benzenes, biphenyls, 2-phenylpyrimidines, phenylbenzoates). Most compounds have rather high melting points. Only molecules with seven aromatic rings show liquid crystalline properties. Two-dimensional modulated smectic phases (rectangular columnar phases) were found for molecules with phenylbenzoate rigid units. Intercalated fluid smectic phases were detected for the corresponding 2-phenylpyrimidine derivatives. For the first time in the case of banana-shaped molecules a nematic phase was observed for a 2′-nitro-*m*-terphenyl-4,4″-diyl bisbenzoate. However, none of the synthesized compounds exhibit the typical texture of the (anti)ferroelectric switchable mesophases, known from the Schiff's base derivatives.

Introduction

Ferroelectricity, resulting from a spontaneous macroscopic electric polarization, is a property which was first reported by Meyer[1] to occur in a fluid, liquid crystalline phase. Until recently, ferroelectricity in liquid crystals was based on a tilted arrangement of homochiral molecules in layers (*e.g.* smectic C phase). Later on, antiferroelectric and ferrielectric phases were also found in nonoracemic chiral S_C materials.[2–4] Such (anti)-ferroelectric liquid crystals have attracted considerable interest because of their exceptional switching properties and their technical applications, for example, in fast-switching electrooptical displays.[5] It was predicted by theory that ferroelectricity and antiferroelectricity should not be restricted to chiral tilted phases.[6–9] For example polyphilic molecules[10] and bowl-shaped molecules[11,12] have been designed to obtain non-chiral ferroelectric fluids.

In 1996 Niori *et al.*[13] reported on ferroelectricity in a smectic phase formed by 'banana-shaped' non-chiral molecules such



I

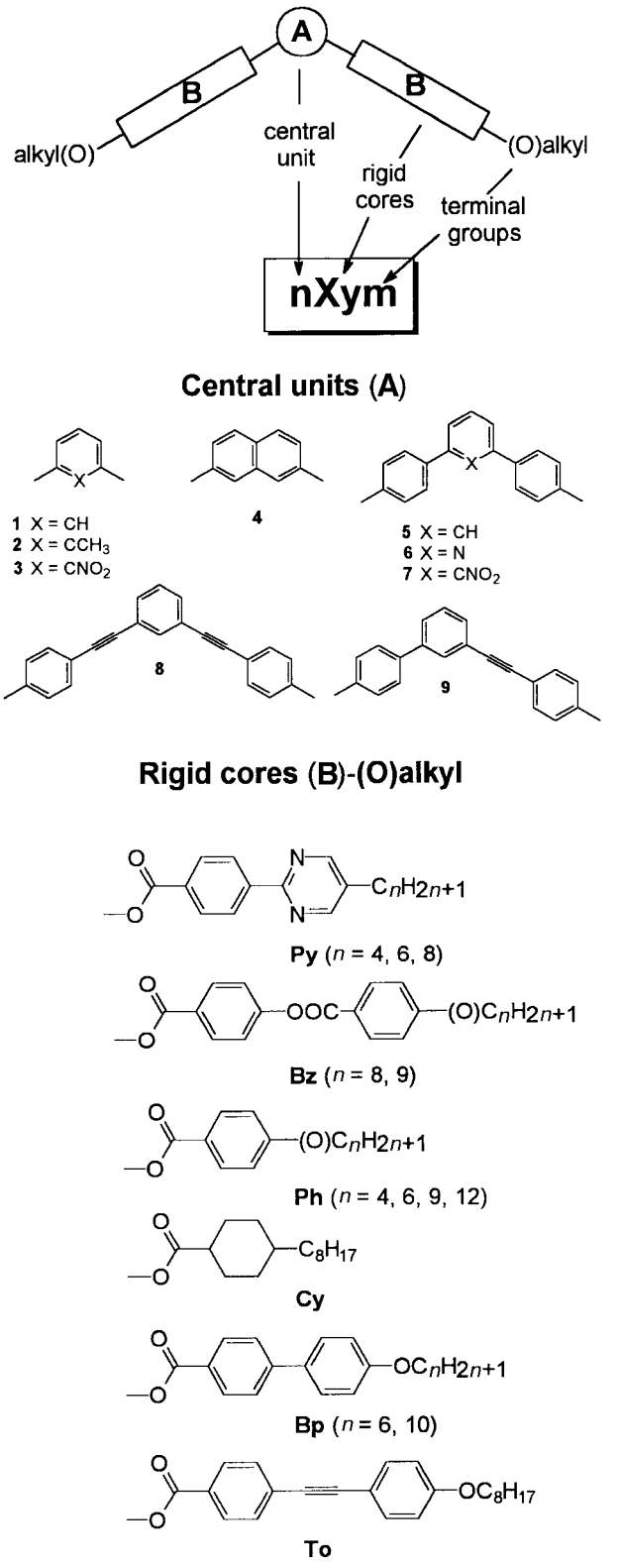
R = C_nH_{2n+1}, OC_nH_{2n+1}

as **I**. Other groups found antiferroelectric switching behavior.[14–16] It was proposed that the source of the special properties is a uniform arrangement of the bent molecules resulting in a structure that possesses C_{2v} symmetry.[16,17] Not only are the special electrooptical behavior of these non-conventional liquid crystals, their potential application as switchable NLO-materials,[18] and the observation of a spontaneous symmetry breaking in some mesophases of these achiral molecules[16,17,19] of interest. Furthermore these molecules represent a new sub-group of thermotropic liquid crystals, different from classical types, such as calamitic and disc-like mesogens. Up to now, all banana-shaped liquid crystals which have exhibited (anti)ferroelectric switching behavior have had a rather uniform structure. Their molecular structure can be regarded as being composed of three units. These are an angular central unit **A**, two linear rigid cores **B** and the terminal chains (see upper part of Scheme 1). The molecules reported up to now have a 1,3-disubstituted benzene ring as the central unit, and in most cases two Schiff's base-containing units as the rigid cores. Therefore, a major drawback of these compounds is their limited thermal, hydrolytic and photochemical stability. Thus, the design of novel, stable and low-melting banana-shaped mesogens is a topical subject in liquid crystal research. Here we describe the synthesis and properties of novel banana-shaped molecules without Schiff's base units.

For this purpose we have combined different rigid angular central units, such as a 1,3-disubstituted benzene unit (**1**), the 1,3-diphenylbenzene unit (**5**) or the 1,3-bis(phenylethynyl)-benzene unit (**8**) with a single 4-substituted benzene ring (**Ph**), with biphenyl (**Bp**), 2-phenylpyrimidine (**Py**) or phenylbenzoate (**Bz**) rigid cores connected *via* ester linkages to the central unit (see Scheme 1). Furthermore, we have studied the influence of heteroatoms (2,6-diphenylpyridines **6**) and substituents in the 2-position of the angular unit (*e.g.* compounds **2, 3** and the 2-nitro-1,3-diphenylbenzene **7**) on their properties. Finally we have synthesized desymmetrized molecules containing a 1-phenyl-3-(phenylethynyl)benzene central unit (compounds **9BzO9** and **9Py8**).

Synthesis

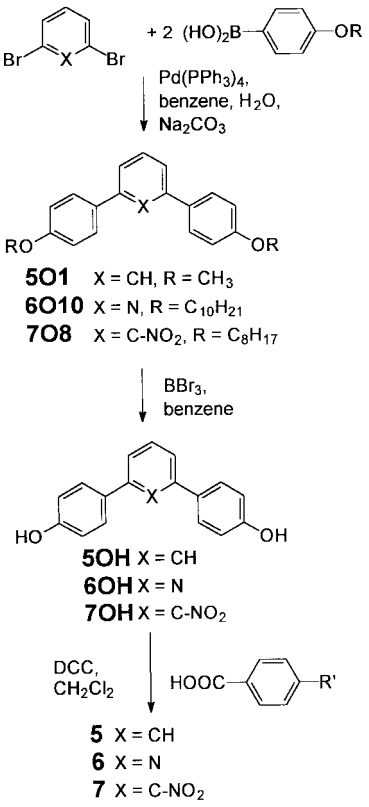
The compounds **1Xym–9Xym** were obtained by esterification of appropriate divalent phenols with 4-(5-alkylpyrimidin-2-yl)benzoic acids[20] (compounds **1Pym–6Pym, 8Py8** and **9Py8**), 4-[4-alkyl(oxy)benzoyloxy]benzoic acids[21] (compounds **5Bzm–9Bzm**), 4-(4-hexyloxyphenyl)benzoic acid[22] (compounds **5BpO6** and **6BpO6**), 4-(4-octyloxyphenylethynyl) benzoic acid[23] (compound **1ToO8**), 4-alkyl(oxy)benzoic acids (compounds **5Phm** and **8Ph8**) or with *trans*-4-octylcyclohexane carboxylic acid (compound **5Cy8**) using the DCC method.



Scheme 1 Structures of the compounds under investigation. The central unit **A** represents the rigid angular central molecular part in which no change of the bending angle is possible.

Resorcinol, 2-nitroresorcinol, 2-methylresorcinol and 2,7-dihydroxynaphthalene were commercially available.

The syntheses of the divalent phenols derived from *m*-terphenyl (X=CH: **5OH**),[24] 2,6-diphenylnitrobenzene (X=$CHNO_2$: **7OH**) and 2,6-diphenylpyridine (X=N: **6OH**) are shown in Scheme 2. Suzuki cross-coupling[25] of 1,3-dibromobenzene, 2,6-dibromopyridine and 2-nitro-1,3-dibromobenzene[26] with 2 equiv. of 4-alkoxyphenylboronic acids gave the



Scheme 2 Synthesis of 1,3-bis(4-hydroxyphenyl)benzene **5OH**, 2,6-bis(4-hydroxyphenyl)pyridine **6OH** and 2,6-bis(4-hydroxyphenyl)-2-nitrobenzene **7OH**.

ethers **5O1**, **6O10** and **7O8** which were cleaved with BBr_3[27] to give the phenols **5OH**, **6OH** and **7OH** respectively. 2-Nitro-1,3-dibromobenzene was obtained from 2,6-dibromoaniline by a two step oxidation, first with MCPBA to give 1,3-dibromo-2-nitrosobenzene,[28] followed by oxidation with nitric acid to give the desired 2-nitro compound.[29]

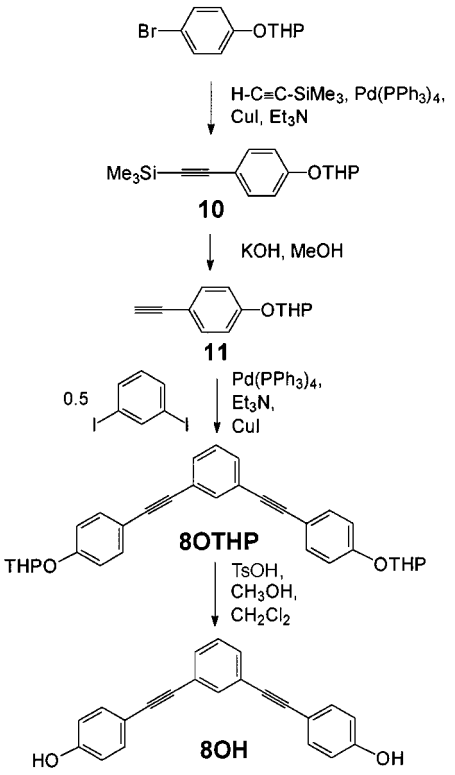
The synthesis of the 1,3-bis(phenylethynyl)benzene derivatives is shown in Scheme 3. Because the triple bond gives rise to serious side reactions during ether cleavage with BBr_3, the tetrahydropyranyl group was used as protective group instead of simple alkyl ethers. 1-Bromo-4-tetrahydropyranyloxybenzene[30] was coupled with trimethylsilylacetylene under the joint influence of $Pd(PPh_3)_4$ and CuI.[31] Cleavage of the C–Si bond was achieved with potassium hydroxide in methanol.[32] The obtained 4-tetrahydropyranyloxyphenylacetylene **11**[23] was cross-coupled with 1,3-diiodobenzene. Acidolytic cleavage of the THP ethers gave the phenol **8OH**.

The desymmetrized phenol **9OH** was obtained by using two subsequent coupling reactions, as shown in Scheme 4. 1-Bromo-3-iodobenzene was first coupled with 4-tetrahydropyranyloxyphenylacetylene (**11**) at the iodo group, followed by Suzuki coupling of the resulting bromobenzene derivative **12** with 4-(*tert*-butyldiphenylsilyloxy)phenylboronic acid. Stepwise deprotection of **13** with tetrabutylammonium fluoride[33] followed by acidolysis gave the desymmetrized phenol **9OH**. All final compounds were purified by column chromatography, followed by repeated crystallization from methanol.

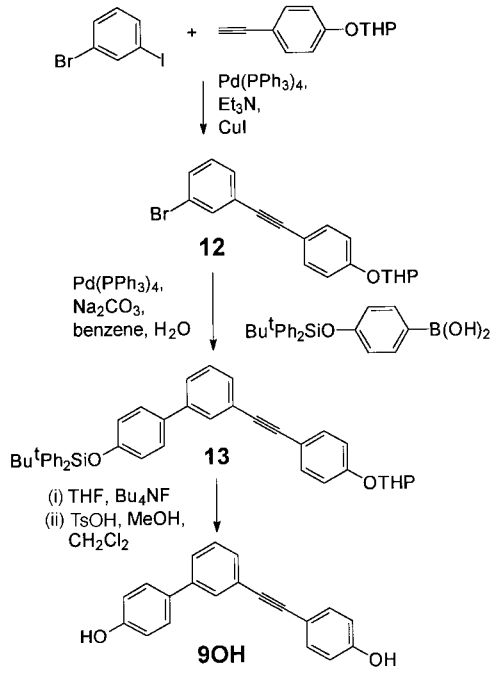
Results and discussion

1,3-Phenylene bisbenzoates

All acylated resorcinols incorporating the 2-phenylpyrimidine rigid core (compounds **1Pym–3Pym**, Table 1) are crystalline



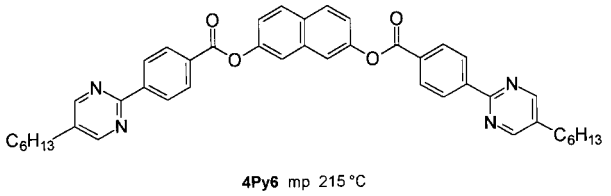
Scheme 3 Synthesis of 1,3-bis(4-hydroxyphenylethynyl)benzene **8OH**.



Scheme 4 Synthesis of 1-(4-hydroxyphenyl)-3-(4-hydroxyphenylethynyl)benzene **9OH**.

solids without mesomorphic properties. These compounds crystallize rapidly on cooling (5–10 K below the melting point) and therefore no monotropic mesophases could be detected.

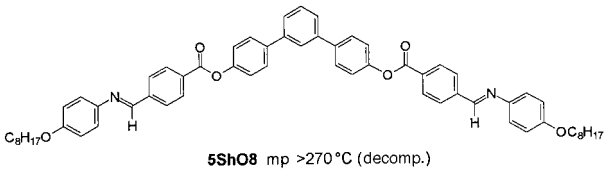
Also the 2,7-dihydroxynaphthalene derivative **4Py6** is a high melting solid without mesomorphic properties. Comparison of the related compounds **1Py6** and **4Py6** shows a significant increase of the melting point on replacing the central benzene unit by a 2,7-disubstituted naphthalene unit. Because of the unfavorable properties provided by these two central units they were not combined with other rigid cores.



4Py6 mp 215 °C

m-Terphenyl derivatives and 2,6-diphenylpyridines

The transition temperatures of the *m*-terphenyl derivatives and 2,6-diphenylpyridines are summarized in Tables 2–5. Compound **5BpO6** incorporating biphenyl rigid cores (Table 2) has a high melting temperature and exhibits only a small range of a liquid crystalline phase with a mosaic-like texture.[34] The high temperature of the existence range inhibits a more detailed investigation. This mesophase is lost if the *m*-terphenyl unit is replaced by a 2,6-diphenylpyridine unit

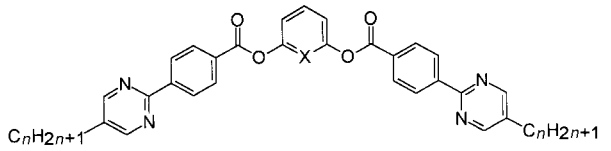


5ShO8 mp >270 °C (decomp.)

(compound **6BpO6**). The Schiff's base derivative **5ShO8** is only a high melting solid which decomposes before melting. Because the high melting temperatures may result from the fact that these molecules incorporate seven aromatic rings, the next aim was to reduce the number of aromatic rings in the rigid units. Although the benzoates **5Phm** (Table 3) incorporating only five benzene rings have significantly lower melting points than the biphenyl derivative **5BpO6**, no mesomorphic properties could be detected, regardless of the chain length. The cyclohexanecarboxylate **5Cy8** has a significantly higher melting point than the benzoates.

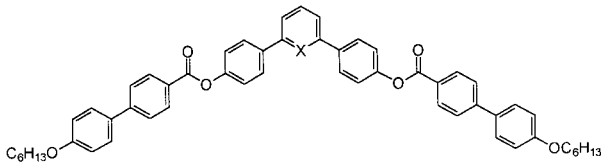
Liquid crystalline phases were found for the phenylbenzoates

Table 1 Melting temperatures of the 4-(5-alkylpyrimidin-2-yl)benzoates **1Pym**, **2Py8** and **3Pym**



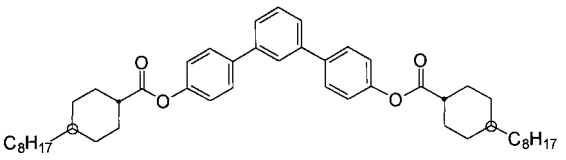
Compound	*n*	X	mp/°C
1Py6	6	CH	160
1Py8	8	CH	130
2Py8	8	CCH_3	166
3Py6	6	CNO_2	145
3Py8	8	CNO_2	106

Table 2 Transition temperatures (T/°C) of the 4-(4-hexyloxyphenyl)-benzoates **5BpO6** and **6BpO6**[a]



Compound	X	Cr		M		Iso
5BpO6	CH	•	258	•	268	•
6BPO6	N	•	268			•

[a]Abbreviations: Cr = crystalline solid, M = unknown mesophase,[34] Iso = isotropic liquid.



5Cy8 mp 168 °C

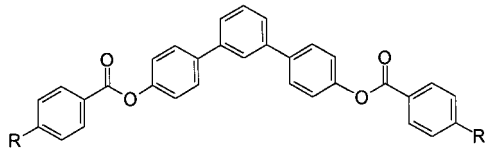
5Bzm–7Bzm (Table 4) and the 2-phenylpyrimidine derivatives **5Pym** and **6Pym** (Table 5). Only the mesophase of compound **6Py8** is monotropic. The other compounds have enantiotropic phases.

The textures of the mesophases of all synthesized *m*-terphenyl derivatives with phenylbenzoate rigid cores (**5Bzm**) and of the corresponding 2,6-diphenylpyridine derivative **6BzO9** (Table 4) are quite similar. As an example the textures of **5BzO9** are shown in the Fig. 1(*a*)–(*c*). On cooling from the isotropic liquid state small batonnets are formed which rapidly turn into branched lancets [Fig. 1(*a*)] and finally coalesce into a structured mosaic-like texture [Fig. 1(*b*)] with some spherulitic domains. This texture was also reported for a frustrated smectic phase of short chain banana-shaped Schiff's base molecules[35] (formula **I**, R = OC_6H_{13}) and was designated as B1.[36] The homeotropic orientation, which can be obtained by shearing thin samples between glass plates, shows always a distinct birefringence. No pseudoisotropic regions can be obtained [Fig. 1(*c*)]. The mesophase of compound **5BzO8** which shows the same texture was investigated by means of X-ray scattering. Four small angle reflections could be detected at the Bragg angles $\Phi_1 = 1.59°$, $\Phi_2 = 1.81°$, $\Phi_3 = 2.98°$ and $\Phi_4 = 3.57°$ which could be indexed as (101), (002), (103) and (004) reflections, respectively, of a centered rectangular two-dimensional lattice as found[35] for the B1 phase. The lattice parameters are $a = 3.37$ nm and $c = 4.86$ nm. The molecular length (L), assuming a bow-shape of the molecule with a bending angle between the two half-parts of *ca.* 120° and an all-*trans* conformation of the alkyl chains, is 5.6 nm. Assuming a ribbon structure as shown in Fig. 2, the parameter c should correspond to the thickness of the ribbons and a may correspond to the diameter of the ribbons in the lateral direction. About seven molecules should be arranged side by side in the ribbons forming the 2D lattice.

The 2′-nitro-substituted *m*-terphenyl derivative **7BzO9** is especially remarkable, because it exhibits an additional nematic phase as a high temperature mesophase (see Fig. 3). The nematic phase was indicated by the schlieren texture and the low transition enthalpy of the transition to the isotropic liquid. Nevertheless, the texture of this nematic phase is slightly different from the nematic phases of conventional calamitic liquid crystals. At first a patterning can be seen (small bright spots in the region of the schlieren texture in Fig. 3). Furthermore it seems that 4-brush-disclinations are missing.[37] Considering the molecular structure a biaxial nematic phase seems not impossible. However, more detailed investigations are necessary to clarify the structure of this nematic phase. At the transition to the low-temperature mesophase the growing of fern-like domains can be seen (see Fig. 3). These domains coalesce to a structured mosaic-like texture with spherulitic domains, quite similar to the two-dimensionally modulated mesophases (B1 phase) of the other compounds incorporating phenylbenzoate rigid cores.

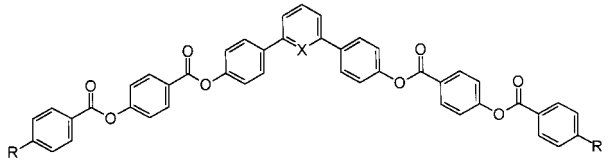
The nematic phase could not be studied by X-ray methods because it exists only at high temperatures, but its existence offers the possibility of obtaining well-oriented samples of the mesophase occurring below the nematic phase. X-Ray studies of these oriented samples gave clear evidence for the existence of a two dimensional rectangular lattice. The lattice parameter $c = 5.24$ nm is nearly independent of the temperature, whereas the parameter a is changed from $a = 3.45$ nm at $T = 150$ °C up

Table 3 Melting temperatures of the 4-alkyl(oxy)benzoates **5Phm**



Compound	R	mp/°C
5Ph4	C_4H_9	135
5Ph6	C_6H_{13}	106
5Ph12	$C_{12}H_{25}$	103
5PhO9	OC_9H_{19}	126

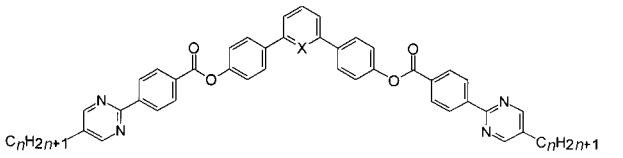
Table 4 Phase transition temperatures (T/°C) and corresponding enthalpy values (lower lines ΔH/kJ mol^{-1} of the *m*-terphenyl-4,4″-diyl bis{4-[4-alkyl(oxy)benzoyloxy]benzoates} **5Bzm** and **7BzO9** and the pyridine-2,6-diylbis(1,4-phenylene) bis[4-(4-nonyloxybenzoyloxy)benzoate] **6BzO9**[a]



Compound	R	X	Cr		B1		N		Iso
5Bz8	C_8H_{17}	CH	•	180[b]	•	207			•
				36.9		20.7			
5BzO8	OC_8H_{17}	CH	•	160	•	226			•
				20.6		22.8			
5BzO9	OC_9H_{19}	CH	•	161	•	219			•
				27.3		25.1			
6BzO9	OC_9H_{19}	N	•	179	•	246			•
				25.5		22.9			
7BzO9	OC_9H_{19}	CNO_2	•	149[c]	•	197	•	217	•
				21.2		10.5		0.4	

[a]Abbreviations: N = nematic phase; B1 = two-dimensionally modulated smectic phase (rectangular columnar mesophase, see Fig. 2); for the other abbreviations, see Table 2. [b]Additional Cr–Cr transition at 173 °C ($\Delta H = 11.3$ kJ mol^{-1}). [c]Additional Cr–Cr transition at 108 °C ($\Delta H = 4.0$ kJ mol^{-1}).

Table 5 Phase transition temperatures (T/°C) and corresponding enthalpy values (lower lines ΔH/kJ mol^{-1}) of the *m*-terphenyl-4,4″-diyl bis[4-(5-alkylpyrimidin-2-yl)benzoate]s **5Pym** and the pyridine-2,6-diylbis(1,4-phenylene) bis[4-(5-alkylpyrimidin-2-yl)benzoate]s **6Py6** and **6Py8**



Compound	n	X	Cr		$S_{intercal}$		B1		Iso
5Py4	4	CH	•	195	•	203			•
				38.6		9.8			
5Py6	6	CH	•	209	•	222			•
				32.4		15.5			
5Py8	8	CH	•	178[b]	•	206			•
				32.1		16.5			
6Py6	6	N	•	224				242	•
				35.5				21.1	
6Py8	8	N	•	231[c]			(•	230)	•
				29.5				11.9	

[a]Abbreviations: $S_{intercal}$ = fluid smectic phase of intercalated molecules; for the other abbreviations see Tables 2 and 4. [b]Additional Cr–Cr transition at 105 °C ($\Delta H = 10.2$ kJ mol^{-1}). [c]Additional Cr–Cr transitions at 131 °C ($\Delta H = 12.9$ kJ mol^{-1}) and 204 °C ($\Delta H = 47.7$ kJ mol^{-1}).

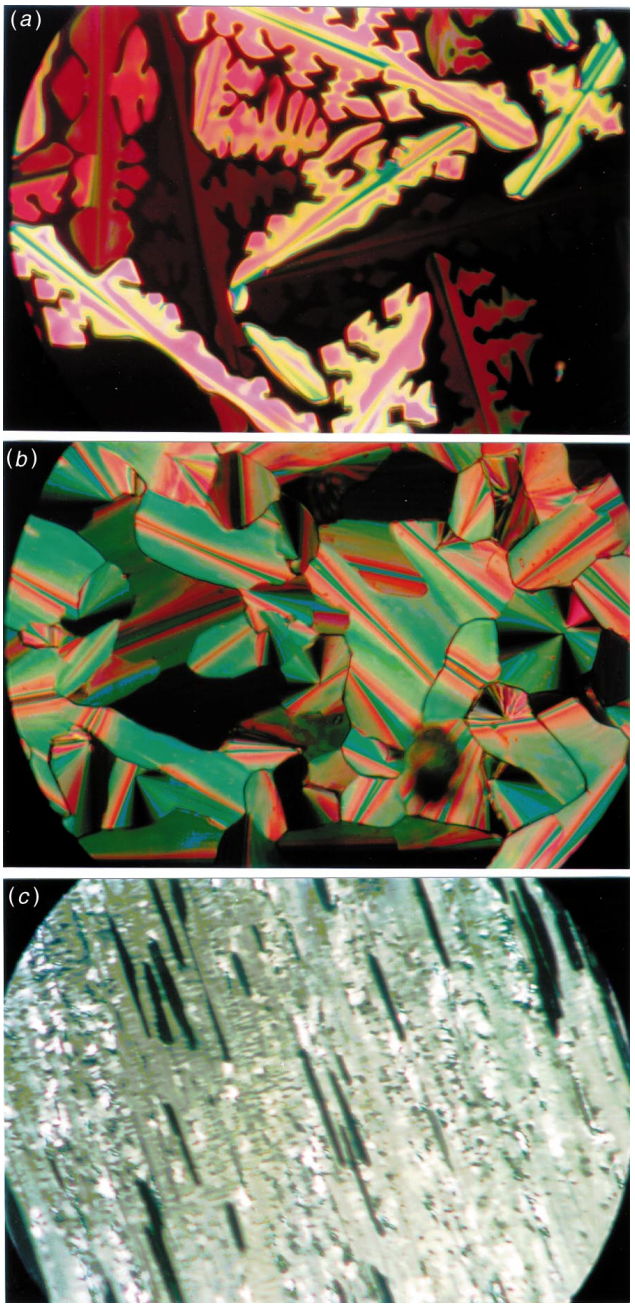


Fig. 1 Optical photomicrographs (crossed polarizers) of compound **5BzO9** (*a*) at the transition from the isotropic liquid state to the mesophase at 219 °C; (*b*) in the B1 phase at 210 °C and (*c*) after shearing the sample at 210 °C.

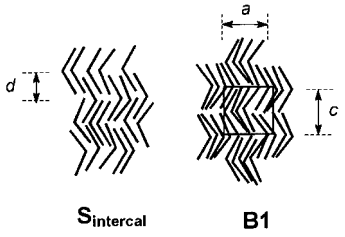


Fig. 2 Arrangement of the molecules in the $S_{intercal}$ phase and in the B1 phase.

to $a = 3.77$ nm at $T = 190$ °C. The molecular length assuming an all-*trans* conformation of the alkyl chains amounts to 5.9 nm ($L/c = 0.89$) and again fits with the parameter c, whereas the parameter a (which describes the lateral distance between the ribbons) is in the same order of magnitude as

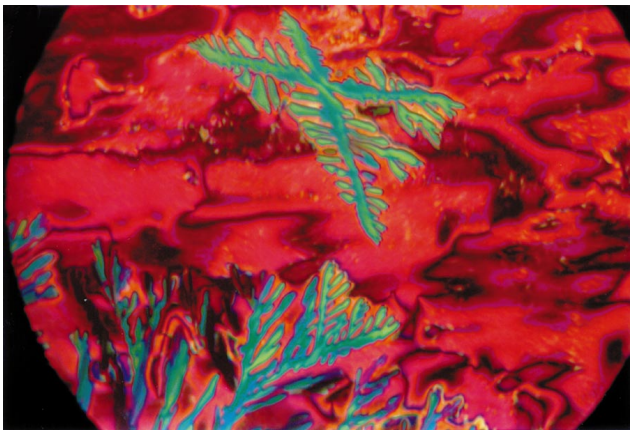


Fig. 3 Optical photomicrograph (crossed polarizers) of the transition from the nematic phase (orange schlieren texture) to the B1 phase (blue dendritic domains) of compound **7BzO9** at 197 °C.

found for the ribbon-phase of compound **5BzO8**. The optical textures of the *m*-terphenyl derivatives incorporating 2-phenylpyrimidine rigid cores (compounds **5Py4, 5Py6** and **5Py8**, see Table 5) are different from those of the corresponding phenylbenzoates. On cooling these compounds from the isotropic liquid state the formation of batonets is observed which coalesce to a fan-texture (see Fig. 4). This mesophase has a significantly lower viscosity than the B1 phases of the corresponding phenylbenzoates and it is impossible to get pseudo-isotropic regions. The homeotropic alignment, which can be obtained by shearing, is birefringent and rapidly turns back into a fan texture. However the typical S_C schlieren texture could not be observed.

The X-ray pattern of the mesophase of **5Py8** exhibits only the (001) reflection (layer reflection with $d = 2.24$ nm) together with the outer diffuse scattering. Comparison with the molecular data ($L = 5.1$ nm assuming again a bending angle of 120°) leads to an intercalated structure of this mesophase (see Fig. 2). The microscopic observations as well as the X-ray data are in agreement with results obtained for intercalated S_C phases of other banana-shaped compounds, designated as B6.[38] In this mesophase a tilt of the molecules with respect to the layer normal was proven.[38] However, comparison of the obtained d value in the mesophase of **5Py8** with the molecular length (bending angle = 120°, all-*trans* conformation of the alkyl chains) gives a ratio $2d/L = 0.88$, which corresponds to the ratios usually obtained for non-tilted S_A phases. This small difference between molecular length ($L/2$) and layer thickness (d) can be explained by the molten liquid state of the alkyl chains and is no indication of a tilted arrangement of the

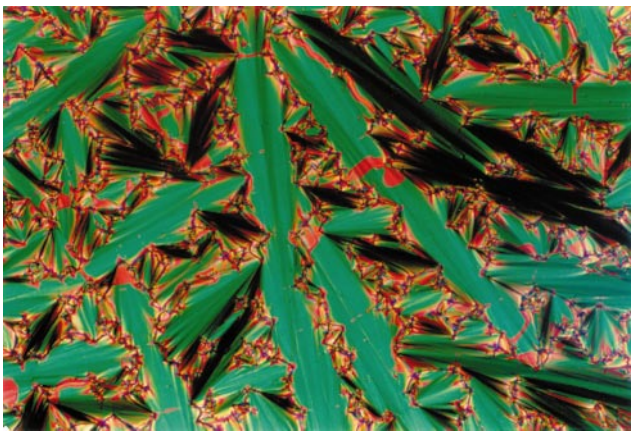


Fig. 4 Optical photomicrograph (crossed polarizers) of the fan texture of the fluid smectic phase of compound **5Py6** obtained on cooling at 194 °C.

molecules. Furthermore, because of the biaxiality of the molecules no pseudoisotropic regions should be possible between crossed polarizers even if the molecules are non-tilted.[39] Because no oriented samples have been obtained in the X-ray experiments we cannot exclude a small tilt ($<30^\circ$) of the molecules.

For the mesophases of the 2-phenylpyrimidine derivatives of 2,6-diphenylpyridine **6Py6** and **6Py8** (Table 5) the same mosaic texture as described for the corresponding phenylbenzoate **6BzO9** and the phenylbenzoates of *m*-terphenyl **5Bzm** was found. It can be assumed that again a phase of B1 type (rectangular columnar ribbon phase) appears, but the crystallization prevents more detailed studies by X-ray methods.

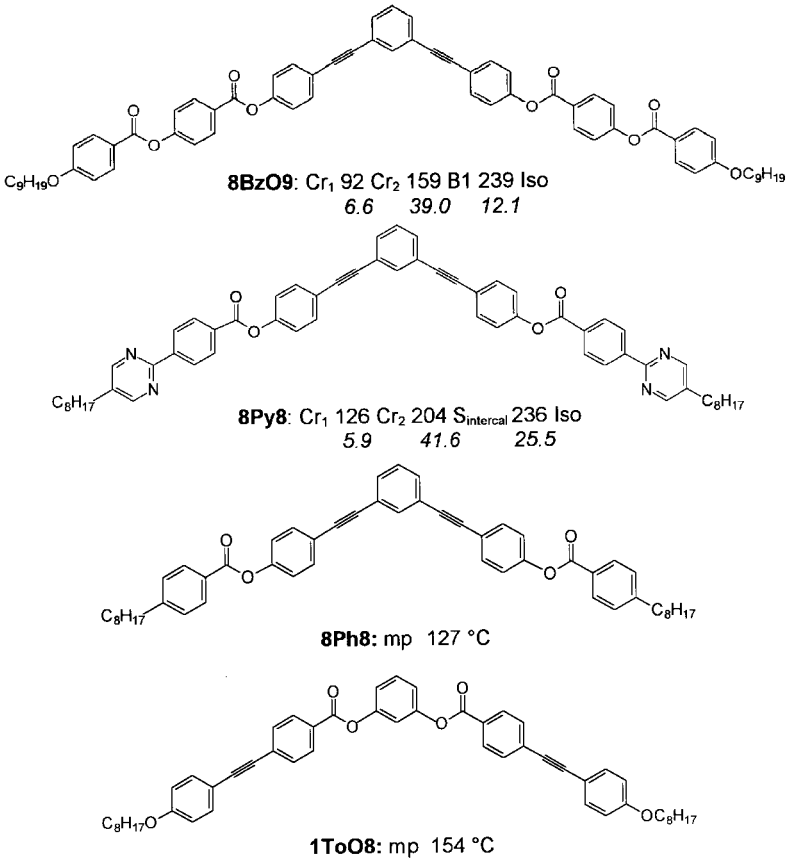
Diphenylacetylene derivatives

Three different types of banana-shaped molecules incorporating the diphenylacetylene unit have also been synthesized. The 1,3-bis(phenylethynyl)benzenes **8Py8** and **8BzO9**, which have two triple bonds connected to the central 1,3-disubstituted benzene ring, behave in a similar manner to the corresponding *m*-terphenyl derivatives without the acetylene units: the compound **8Py8** incorporating 2-phenylpyrimidine rigid cores shows an S_C-like texture of the intercalated smectic phase and the phenylbenzoate **8BzO9** displays the typical texture of a two-dimensionally modulated smectic phase as found for the corresponding *m*-terphenyl derivatives (see Fig. 1). Comparison with the *m*-terphenyl derivatives **5Py8** (see Table 5) and **5BzO9** (see Table 4) indicates that the clearing temperatures are enhanced by about 20–30 K by introduction of the C≡C triple bond, whereas the influence on the melting temperatures is quite different.

Also in the case of these acetylene derivatives it was not possible to reduce the number of aromatic rings incorporated in the molecules without loss of the mesomorphic properties. The benzoate **8Ph8** is a crystalline solid which can be supercooled to 120 °C without formation of a mesophase. Also shifting the position of the acetylenic units from the central part to the rod-like rigid units (see compound **1ToO8** with tolane rigid cores) does not give rise to liquid crystalline phases.

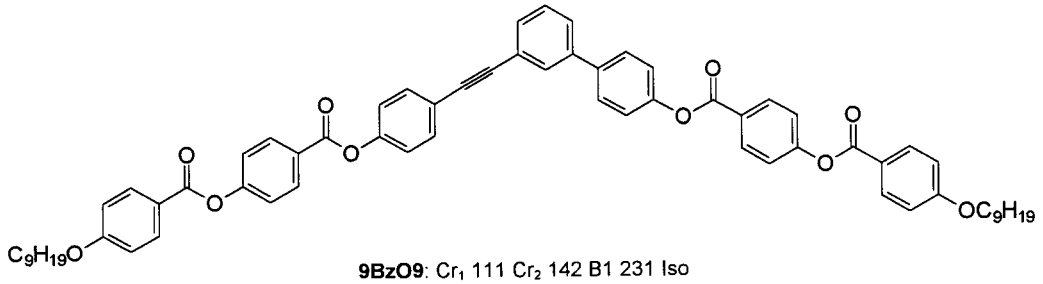
A main disadvantage of all compounds reported herein is their rather high melting temperature. In order to overcome this we set out to synthesize desymmetrized banana-shaped molecules. The 1-phenyl-3-(4-phenylethynyl)benzene derivatives **9BzO9** and **9Py8** connect two molecular parts of different length (regarding the 1,3-disubstituted benzene ring as the central unit). This leads to lower melting points in comparison to the corresponding 1,3-bis(phenylacetylene)benzenes **8Py8** and **8BzO9**, whereas the phase type seems to be unchanged, which means that the 2-phenylpyrimidine derivative **9Py8** exhibits the texture of the intercalated fluid smectic phase whereas a texture typical for the two-dimensional modulated smectic phases was found for **9BzO9**.

Also the powder-like X-ray pattern of **9BzO9** supports this conclusion. Two small angle reflections ($d_1 = 2.88$ nm, $d_2 = 2.63$ nm at $T = 165\,^\circ$C) prove the existence of a two-dimensional cell. Assuming again a rectangular cell the parameters $c = 5.26$ nm and $a = 3.58$ nm can be calculated, which are quite similar to those found for compounds **5BzO8** and **7BzO9**.

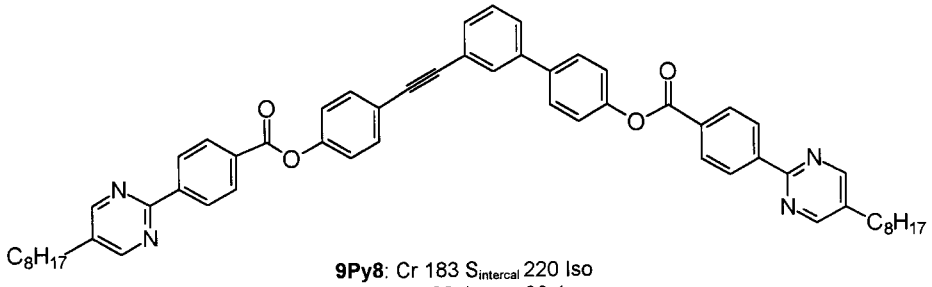


Conclusions

This paper reports attempts to form (anti)ferroelectric switchable achiral banana-shaped molecules without Schiff's base units. Therefore, several novel V-shaped molecules consisting of different angular central units and linear rigid units have been synthesized. Most compounds have very high melting points. Only molecules with seven aromatic rings show liquid crystalline properties. Three different types of mesophases have been found: phases with a two-dimensional modulated layer structure (rectangular columnar phases, ribbon phases) designated as B1, intercalated fluid smectic phases $S_{intercal}$ and—for the first time in the case of banana-shaped



9BzO9: Cr_1 111 Cr_2 142 B1 231 Iso
2.2 21.5 21.1



9Py8: Cr 183 $S_{intercal}$ 220 Iso
38.1 20.1

molecules—a nematic phase. Although a wide variety of chemically different molecules have been screened, none of them shows the typical texture of the (anti)ferroelectric switchable mesophases B2, known for the Schiff's base derivatives.[40]

Obviously the occurrence of liquid crystalline phases in this class of banana-shaped compounds is very sensitive to slight changes in the chemical structure. To date, no concepts concerning the general structure–property relationships of this subtype of mesogens exist. This situation is reminiscent of the early days of calamitic and discotic liquid crystals. Therefore, further structural variations are necessary to uncover the fundamental design principles of this new class of thermotropic mesogens.

Experimental

General

Confirmation of the structures of the intermediates and products was obtained by ^{1}H NMR spectroscopy (Varian Unity 500, Varian Gemini 200 spectrometer) (*J* values given in Hz). Mass spectra were recorded on an AMD 402 mass spectrometer (70 eV). The purity of all compounds was checked by thin-layer chromatography. Microanalyses were performed using a Leco CHNS-932 elemental analyzer. Transition temperatures were measured using a Mettler FP 82 HT hot stage and control unit in conjunction with a Nikon Optiphot-2 polarizing microscope and were confirmed using a differential scanning calorimeter (Perkin-Elmer DSC-7). X-Ray studies were performed by means of a Guinier goniometer (Fa. Huber).

Synthesis of 1,3-bis(4-hydroxyphenyl)benzene 5OH

1,3-Bis(4-methoxyphenyl)benzene 5O1. 4-Methoxyphenylboronic acid (0.8 g, 5.3 mmol) was added to a solution of 1,3-dibromobenzene (0.52 g, 2.2 mmol) in a mixture of benzene (12 ml) and aqueous sodium carbonate (2 M, 12 ml) at room temperature under an argon atmosphere, and $Pd(PPh_3)_4$ (0.1 g, 0.1 mmol, 5 mol%) was then added to the mixture. The mixture was heated under reflux with stirring for 4 h. Afterwards the solution was extracted with CH_2Cl_2 (2×150 ml) and dried with Na_2SO_4. The solvent was removed and the product was purified by column chromotography ($CHCl_3$), and then recrystallized from *n*-hexane. Yield 0.55 g (86.2%); mp 198–200 °C (lit.,[24] 197–198 °C); δ_H($CDCl_3$; 400 MHz) 7.72 (d, *J* 1.45, 1H, Ar-H), 7.58 (d, *J* 8.9, 4H, Ar-H), 7.51–7.44 (m, 3H, Ar-H), 7.00 (d, *J* 8.9, 4H, Ar-H), 3.86 (s, 6H, OCH_3).

1,3-Bis(4-hydroxyphenyl)benzene 5OH. 5O1 (0.55 g, 1.9 mmol) was dissolved in dry benzene (158 ml) and then BBr_3 (2.37 g, 9.4 mmol) was carefully added at room temperature with stirring to the solution; the solution was refluxed for 2 h and then cooled to room temperature. Water (50 ml) was slowly added and the white crystals were collected. The product was crystallized from MeOH. Yield 0.35 g (70.0%); mp 182–183 °C (lit.,[24] 182–183 °C); δ_H(DMSO-d_6; 200 MHz) 9.53 (s, 2H, OH), 7.70 (s, 1H, Ar-H), 7.57–7.43 (m, 7H, Ar-H), 6.85 (d, *J* 8.6, 4H, Ar-H).

Synthesis of 2,6-bis(4-hydroxyphenyl)pyridine 6OH

2,6-Bis(4-decyloxyphenyl)pyridine 6O10. Synthesized as described for the preparation of compound **5O1**. Quantities: 4-decyloxyphenylboronic acid (1.46 g, 5.3 mmol), 2,6-dibromopyridine (0.52 g, 2.2 mmol), $Pd(PPh_3)_4$ (0.11 g, 0.11 mmol, 5 mol%), benzene (11 ml), Na_2CO_3 (2 M, 11 ml). Yield 0.9 g (75.6%); mp 132–133 °C; δ_H($CDCl_3$; 200 MHz) 8.08 (d, *J* 9.0, 4H, Ar-H), 7.78 (t, 1H, Ar-H), 7.58 (d, *J* 8.0, 2H, Ar-H), 7.02 (d, *J* 9.0, 4H, Ar-H), 4.03 (t, *J* 6.5, 4H, OCH_2), 1.85–1.75 (m, 4H, OCH_2CH_2), 1.52–1.44 (m, 28H, CH_2), 0.89 (t, *J* 6.5, 6H, CH_3).

2,6-Bis(4-hydroxyphenyl)pyridine 6OH. Synthesized as described for the preparation of compound **5OH**. Quantities: 2,6-bis(4-decyloxyphenyl)pyridine **6O10** (0.5 g, 0.92 mmol), benzene (70 ml), BBr_3 (1.15 g, 4.58 mmol). Yield 0.18 g (75.0%); mp >265 °C; δ_H(DMSO-d_6; 200 MHz) 8.00 (d, *J* 8.8, 4H, Ar-H), 7.76 (d, 2H, *J* 7.6, Ar-H), 7.20 (t, 1H, *J* 7.6, Ar-H), 6.90 (d, *J* 8.8, 4H, Ar-H).

Synthesis of 2,6-bis(4-hydroxyphenyl)nitrobenzene 7OH

2,6-Dibromonitrobenzene. 2,6-Dibromoaniline (1.26 g, 5.0 mmol) and 3-chloroperoxybenzoic acid (3.85 g, 22.3 mmol) were dissolved in CH_2Cl_2 (35 ml). The solution was heated under reflux for 2 h, then cooled to room temperature. The precipitate (3-chlorobenzoic acid) was filtered off. The solution was extracted with aqueous 1 M KOH (50 ml) until no 3-chloroperoxybenzoic acid could be detected by TLC (silica gel, $CHCl_3$). The solvent was removed and the obtained

2,6-dibromonitrosobenzene was recrystallized from *n*-hexane. Yield 1.10 g (83.0%); mp 132–133 °C (lit.,[28] 134–135 °C); ν_{max}(KBr)/cm^{-1} 1548, 1423, 1274, 804; *m*/*z* (70 eV) 265 (M^+, 100%), 235 (85), 154 (25).

2,6-Dibromonitrosobenzene (1.23 g, 4.64 mmol) was dissolved in glacial acetic acid (25 ml), and a solution of H_2O_2 (a mixture of 12.5 ml of a 33% solution in water and 12.5 ml glacial acetic acid) was added at room temperature. Then HNO_3 (0.83 ml) was added. The mixture was heated in a water bath to 90 °C, until the color of the solution turned to orange (1 h). Water (52 ml) was added, and the formed solid was separated. The product obtained was crystallized from *n*-hexane. Yield 1.13 g (86.9%); mp 78–79 °C (lit.,[29] 82 °C); ν_{max}(KBr)/cm^{-1} 1548, 1523, 1400, 780; *m*/*z* (70 eV) 280 ($[M-1]^+$, 45%), 251 (37), 234 (28), 223 (37), 156 (30), 75 (100).

2,6-Bis(4-octyloxyphenyl)nitrobenzene 7O8. Synthesized as described for the preparation of compound **5O1**. Quantities: 2,6-dibromonitrobenzene (1.06 g, 3.77 mmol), 4-octyloxyphenylboronic acid (2.26 g, 9.05 mmol), benzene (19 ml). Na_2CO_3 (2 M, 19 ml), $Pd(PPh_3)_4$ (0.2 g, 0.2 mmol, 5 mol%), purified by column chromatography ($CHCl_3$), light yellow oil. Yield 1.48 g (74.0%); δ_H($CDCl_3$; 200 MHz) 7.65–7.25 (m, 6H, Ar-H), 7.00–6.90 (m, 5H, Ar-H), 3.96 (m, 4H, OCH_2), 1.80–1.30 (m, 24H, CH_2), 0.90 (t, *J* 6.3, 6H, CH_3).

2,6-Bis(4-hydroxyphenyl)nitrobenzene 7OH. Synthesized as described for the preparation of compound **5OH**. Quantities: **7O8** (2.38 g, 4.48 mmol), benzene (237 ml), BBr_3 (4.6 g, 18.3 mmol). Yield 1.10 g (80.0%); mp >265 °C; δ_H(DMSO-d_6; 400 MHz) 9.72 (s, 2H, OH), 7.62 (t, *J* 7.6 1H, Ar-H), 7.42 (d, *J* 7.6, 2H, Ar-H), 7.14 (d, *J* 8.8, 4H, Ar-H), 6.81 (d, *J* 8.8, 4H, Ar-H).

Synthesis of 8OH and 9OH

1 - Bromo - 4 - tetrahydropyranyloxybenzene. To a stirred solution of 4-bromophenol (10.0 g, 57.8 mmol) in CH_2Cl_2 (35 ml), cooled with an ice bath, dihydropyran (6.0 g, 0.07 mol) was added dropwise over 10 min at 0–5 °C. After the solution became clear, TsOH (10 mg) was added. The solution was stirred at 20 °C for 15 min. Then it was quenched by addition of $NaHCO_3$ (0.7 g) and 3 drops of water, and after stirring for 5 min at 20 °C the solvent was removed *in vacuo* and the product obtained was purified by column chromatography ($CHCl_3$). Yield 14.0 g (94.2%); mp 54–55 °C (lit.,[30] 55–56 °C); δ_H($CDCl_3$; 200 MHz) 7.35 (d, *J* 9.0, 2H, Ar-H), 6.92 (d, *J* 9.0, 2H, Ar-H), 5.35 (t, *J* 3.0, 1H, OCHO), 3.85 (m, 1H, THP), 3.61 (m, 1H, THP), 2.10–1.50 (m, 6H, THP).

4 - Tetrahydropyranyloxy - 1 - (trimethylsilylethynyl) benzene 10.[23] A stirred mixture of 1-bromo-4-tetrahydropyranyloxybenzene (5.65 g, 22.0 mmol), trimethylsilylacetylene (2.24 g, 22.9 mmol), copper(I) iodide (0.22 g, 1.15 mmol) and tetrakis(triphenylphosphine)palladium(0) (1.26 g, 1.26 mmol) in dry triethylamine (70 ml) was refluxed under an argon atmosphere for 19 h. After cooling to room temperature diethyl ether (100 ml) and water (100 ml) were added and the aqueous layer was washed with diethyl ether (2 × 100 ml). The combined etheral extracts were washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo* and the residue was purified by column chromatography (*n*-hexane–ethyl acetate = 9 : 1) to give a yellow–brown oil. Yield 4.47 g (74.2%); δ_H($CDCl_3$; 200 MHz) 7.37 (d, *J* 9.0, 2H, Ar-H), 6.95 (d, *J* 9.0, 2H, Ar-H), 5.35 (t, 1H, OCHO), 3.85 (m, 1H, THP), 3.61 (m, 1H, THP), 2.00–1.50 (m, 6H, THP), 0.22 (s, 9H, CH_3).

4-Tetrahydropyranyloxyphenylacetylene 11. An aqueous solution of potassium hydroxide (1.0 M, 21.0 ml) was added dropwise to a stirred solution of **10** (4.47 g, 16.3 mmol) in MeOH (175 ml) at room temperature. The solution was stirred at this temperature for 1.5 h. Water (100 ml) was added, the aqueous layer was separated and washed with diethyl ether (2 × 150 ml), the combined etheral extracts were washed with brine (100 ml) and dried with $MgSO_4$. The solvent was removed *in vacuo* to yield a yellow solid. Yield 2.9 g (88.0%); mp 64–65.0 °C (lit.,[23] 65.5 °C); δ_H($CDCl_3$; 200 MHz) 7.42 (d, *J* 9.0, 2H, Ar-H), 6.98 (d, *J* 9.0, 2H, Ar-H), 5.43 (t, 1H, OCHO), 3.88 (m, 1H, THP), 3.64 (m, 1H, THP), 2.99 (s, 1H, C≡CH), 1.90–1.50 (m, 6H, THP).

1 , 3 - Bis (4 - tetrahydropyranyloxyphenylethynyl) benzene 8OTHP. Synthesized in analogy to the preparation of compound **10**, but the reaction mixture was stirred at room temperature for 3 h. Quantities: 1,3-diiodobenzene (1.79 g, 5.42 mmol), **11** (2.18 g, 10.79 mmol), CuI (0.22 g, 1.15 mmol), $Pd(PPh_3)_4$ (0.64 g, 0.64 mmol), Et_3N (68 ml). Yield 1.4 g (54.3%); mp 136–137 °C; δ_H($CDCl_3$; 200 MHz) 7.67 (s, 1H, Ar-H), 7.48–7.34 (m, 7H, Ar-H), 7.02 (d, *J* 9.0 4H, Ar-H), 5.46 (m, 2H, THP), 4.10–3.60 (m, 4H, THP), 1.91–1.64 (m, 12H, THP).

1,3-Bis(4-hydroxyphenylethynyl)benzene 8OH. **8OTHP** (1.4 g, 2.9 mmol) was dissolved in a mixture of CH_2Cl_2 (38 ml) and MeOH (27 ml). To this solution TsOH (0.07 g) was added, and the mixture was stirred at room temperature for 1 h. The solvent was evaporated and the pure compound was obtained by column chromatography ($CHCl_3$–MeOH = 10 : 1), followed by crystallization from CH_2Cl_2. Yield 0.75 g (83.4%); mp 207–208 °C; δ_H($CDCl_3$; 200 MHz) 10.0 (s, 2H, OH), 7.62 (s, 1H, Ar-H), 7.49–7.43 (m, 7H, Ar-H), 6.82 (d, *J* 8.6, 4H, Ar-H).

1-Bromo-3-(4-tetrahydropyranyloxyphenylethynyl)benzene 12. Synthesized as described for the preparation of compound **10**. Quantities: 1-bromo-3-iodobenzene (3.54 g, 12.5 mmol), **11** (2.53 g, 12.5 mmol), CuI (0.19 g, 1.0 mmol), $Pd(PPh_3)_4$ (0.54 g, 0.54 mmol), triethylamine (58 ml), 10 h. Yield, 3.4 g (76.3%); mp 42–43 °C; δ_H($CDCl_3$; 500 MHz) 7.64 (s, 1H, Ar-H), 7.44–7.38 (m, 4H, Ar-H), 7.18 (t, *J* 7.9, 1H, Ar-H), 7.01 (d, *J* 8.8, 2H, Ar-H), 5.43 (t, *J* 3.1 1H, OCHO), 3.87 (m, 1H THP), 3.61 (m, 1H, THP), 2.00–1.50 (m, 6H, THP).

4-(*tert*-Butyldiphenylsilyloxy)phenylboronic acid. 4-Bromophenol (8.65 g, 50 mmol) was dissolved in dry DMF (70 ml). Under an argon atmosphere imidazole (13.6 g, 200 mmol) was then added with stirring. The mixture was cooled with an ice bath while *tert*-butyldiphenylsilyl chloride (16.45 g, 60 mmol) was added dropwise at 0 °C. The mixture was stirred at room temperature for an additional 12 h. Then H_2O (20 ml) and diethyl ether (125 ml) were added and the organic phase was separated. The aqueous phase was extracted three times with diethyl ether (3 × 100 ml), the combined organic phases were washed with H_2O (3 × 40 ml) and brine (40 ml) and dried with Na_2SO_4. Then the solvent was removed and the 1-bromo-4-(*tert*-butyldiphenylsilyloxy)benzene was purified by column chromatography [light petroleum (80–110 °C)–ethyl acetate = 9 : 1]. Yield 20.9 g, mp 46–48 °C.

A solution of 1-bromo-4-(*tert*-butyldiphenylsilyloxy)benzene (10.52 g, 25.6 mmol) in dry THF (200 ml) was cooled with violent stirring to −78 °C. BuLi (22 ml of a 1.6 mol dm^{-3} solution in hexane, 35.2 mmol) was added dropwise. The suspension was stirred at −78 °C for an additional 3 h and then trimethyl borate (5.4 g, 51.9 mmol) was added *via* a syringe. The temperature was kept below −70 °C during the addition. The reaction mixture was stirred overnight and was allowed to warm up to room temperature during this time.

After the addition of hydrochloric acid (120 ml, 3 mol dm^{-3}), the mixture was stirred for an additional hour at 20 °C. Afterwards it was extracted with diethyl ether (2 × 200 ml). The combined organic phases were washed with water (100 ml) and dried with Na_2SO_4. After evaporation of the solvent the residue was recrystallized from light petroleum. Yield 8.9 g (92.7%); mp 164–170 °C; δ_H($CDCl_3$; 200 MHz) 7.86 (d, *J* 8.4, 2H, Ar-H), 7.71 (m, 4H, Ar-H), 7.49–7.34 (m, 6H, Ar-H), 6.81–6.75 (m, 2H, Ar-H), 1.10 (s, 9H, CH_3).

1-[4-(*tert*-Butyldiphenylsilyloxy)phenyl]-3-(4-tetrahydropyranyloxyphenylethynyl)benzene 13. Synthesized as described for the preparation of compound **5O1**. Quantities: **12** (2.0 g, 5.62 mmol), 4-(*tert*-butyldiphenylsilyloxy)phenylboronic acid (2.53 g, 6.73 mmol), $Pd(PPh_3)_4$ (0.3 g), benzene (30 ml), Na_2CO_3 (2 M, 30 ml). Yield 1.93 g (56.5%); mp 142–143 °C; δ_H($CDCl_3$; 200 MHz) 7.75–7.00 (2d, 4H, Ar-H), 7.62 (s, 1H, Ar-H), 7.45–7.30 (m, 13H, Ar-H), 7.02–6.78 (2d, 4H, Ar-H), 5.42 (t, 1H, *J* 3.1 OCHO), 3.84 (m, 1H, THP), 3.59 (m, 1H, THP), 2.00–1.50 (m, 6H, THP), 1.10 (s, 9H, CH_3).

1-(4-Hydroxyphenyl)-3-(4-tetrahydropyranyloxyphenylethynyl)benzene 14. 13 (1.45 g, 2.5 mmol) was dissolved in dry THF (45 ml), Bu_4NF (5.0 ml, 1 M THF) was added, and the mixture was stirred at room temperature for 10 h. Afterwards the solvent was removed and $CHCl_3$ (60 ml) and H_2O (40 ml) were added. The organic phase was washed with water (20 ml) and dried with Na_2SO_4. The product was purified by column chromatography (light petroleum–ethyl acetate = 10:4). Yield 0.5 g (56.8%); mp 82–87 °C; δ_H($CDCl_3$; 200 MHz) 7.68 (d, *J* 1.6, 1H, Ar-H), 7.49–7.31 (m, 7H, Ar-H), 7.01 (d, *J* 8.8, 2H, Ar-H), 6.89 (d, *J* 8.6, 2H, Ar-H), 5.43 (t, *J* 2.8, 1H, OCHO), 3.88 (m, THP), 3.63 (m, THP), 2.03–1.25 (m, 6H, THP).

1-(4-Hydroxyphenyl)-3-(4-hydroxyphenylethynyl)benzene 9OH. Synthesized as described for the preparation of compound **8OH**. Quantities: **14** (0.5 g, 1.35 mmol), CH_2Cl_2 (16 ml), MeOH (10 ml), TsOH (0.03 g). Yield 0.2 g (51.7%); mp 158–160 °C; δ_H(DMSO-d_6; 200 MHz) 9.90 (s, 1H, OH), 9.58 (s, 1H, OH), 7.70–7.36 (m, 8H, Ar-H), 6.89–6.76 (m, 4H, Ar-H).

Synthesis of the 4-(5-alkylpyrimidin-2-yl)benzoic acids Py4, Py6 and Py8

4-(5-Octylpyrimidin-2-yl)benzoic acid Py8. $POCl_3$ (3.4 ml, 37.1 mmol) was added dropwise to DMF (3.4 g, 46.2 mmol) with stirring at 0–5 °C (ice bath), the mixture was then allowed to warm up to 20 °C and was stirred at this temperature for 15 min. A solution of 1,1-dimethoxydecane (5.1 g, 25.0 mmol) in DMF (12.5 ml) was added at room temperature. The mixture was stirred at 20 °C for an additional 3 h. 4-Amidinobenzamide hydrochloride (5.0 g, 26.7 mmol) was added and the resulting suspension was stirred at 20 °C for 1 h. Triethylamine (27.5 ml, 0.2 mmol) followed by DMF (17.5 ml) were slowly added at 20–25 °C. After that the solvent and Et_3N were distilled off *in vacuo* ($T < 100$ °C). The residue was cooled to room temperature and poured into ice-water (150 ml). The yellow solid was filtered off, and purified by column chromatography ($CHCl_3$–MeOH = 10:1). The 4-(5-octylpyrimidin-2-yl)benzamide obtained was crystallized from MeOH. Yield 0.67 g (8.6%), mp 118–120 °C; δ_H($CDCl_3$; 200 MHz) 8.64 (s, 2H, pyrimidine-H), 8.52 (d, *J* 8.6, 2H, Ar-H), 7.74 (d, *J* 8.6, 2H, Ar-H), 2.63 (t, *J* 7.6, 2H, pyrimidine-CH_2), 1.68–1.30 (m, 12H, CH_2), 0.86 (t, *J* 6.4, 3H, CH_3).

4-(5-Octylpyrimidin-2-yl)benzamide (0.67 g, 2.15 mmol) was suspended in H_2O (3 ml), and glacial acetic acid (10 ml) and H_2SO_4 (3 ml) were added. The solution was refluxed for 12 h, cooled to room temperature, and afterwards poured into ice-water (100 ml). The precipitate obtained was crystallized from a MeOH–H_2O mixture (95:5). Yield 0.55 g (82.1%); mp 218–221 °C; δ_H($CDCl_3$; 200 MHz) 8.67 (s, 2H, pyrimidine-H), 8.52 (d, *J* 8.6, 2H, Ar-H), 8.20 (d, *J* 8.6, 2H, Ar-H), 2.64 (t, *J* 7.6, 2H, pyrimidine-CH_2), 1.66–1.19 (m. 12H, CH_2), 0.86 (t, *J* 6.5, 3H, CH_3).

4-(5-Butylpyrimidin-2-yl)benzoic acid Py4. Synthesized as described for the preparation of compound **Py8**. Quantities: 1,1-dimethoxyhexane (19.4 g, 0.13 mol), 4-amidinobenzamide hydrochloride (21.0 g, 0.112 mol). Yield 10.52 g (36.7%); mp 229–230 °C; δ_H(DMSO-d_6; 400 MHz) 8.80 (s, 2H, pyrimidine-H), 8.45 (d, *J* 8.6, 2H, Ar-H), 8.05 (d, *J* 8.6, 2H, Ar-H), 2.62 (m, 2H, CH_2), 1.59 (m, 2H, CH_2), 1.33 (m, 2H, CH_2), 0.90 (t, *J* 7.3, CH_3).

4-(5-Hexylpyrimidin-2-yl)benzoic acid Py6. Synthesized as described for the preparation of compound **Py8**. Quantities: 1,1-dimethoxyoctane (8.7 g, 50 mmol), 4-amidinobenzamide hydrochloride (10.0 g, 50 mmol). Yield 2.24 g (15.8%); mp 224–226 °C; δ_H(DMSO-d_6; 400 MHz) 8.80 (s, 2H, pyrimidine-H), 8.45 (d, *J* 8.6, 2H, Ar-H), 8.05 (d, *J* 8.6, 2H, Ar-H), 2.63 (t, *J* 7.7, 2H, pyrimidine-CH_2), 1.63–1.57 (m, 2H, CH_2), 1.28–1.26 (m, 6H, CH_2), 0.84 (t, *J* 6.9, 3H, CH_3).

General procedure for the esterification of the phenols

The appropriate phenol (0.9 mmol), the benzoic acid (2.0 mmol), DCC (2.1 mmol) and 4-(dimethylamino)pyridine (0.4 mmol) were dissolved in dry CH_2Cl_2 (15 ml), the mixture was stirred at room temperature for 12 h, then water (20 ml) was added and the organic phase was separated. After evaporation of the solvent the product was purified by column chromatography ($CHCl_3$–MeOH = 10:0.5), and then recrystallized from ethyl acetate.

1,3-Phenylene bis[4-(5-hexylpyrimidin-2-yl)benzoate] 1Py6. Synthesized from 1,3-dihydroxybenzene (0.1 g, 0.9 mmol) and **Py6** (0.5 g, 1.8 mmol). Yield 0.18 g (31.0%); mp 160 °C (Found: C, 74.83; H, 6.76; N, 8.91%; $C_{40}H_{42}N_4O_4$ requires C, 74.77; H, 6.54; N, 8.72%); δ_H($CDCl_3$; 200 MHz) 8.69 (s, 4H, pyrimidine-H), 8.57 (d, *J* 8.8 4H, Ar-H), 8.32 (d, *J* 8.8, 4H, Ar-H), 7.50 (t, 1H, Ar-H), 7.26–7.25 (m, 3H, Ar-H), 2.65 (t, *J* 7.7, pyrimidine-CH_2), 1.80–1.35 (m, 16H, CH_2), 0.90 (t, *J* 6.8, 6H, CH_3); *m/z* (70 eV) (%) 642 (M^+, 26%), 267 (100), 239 (8), 168 (9).

1,3-Phenylene bis[4-(5-octylpyrimidin-2-yl)benzoate] 1Py8. Synthesized from 1,3-dihydroxybenzene (0.1 g, 0.9 mmol) and **Py8** (0.55 g, 1.8 mmol). Yield 0.4 g (63.7%); mp 130 °C; δ_H($CDCl_3$; 200 MHz) 8.70 (s, 4H, pyrimidine-H), 8.59 (d, *J* 8.4 4H, Ar-H), 8.32 (d, *J* 8.4, 4H, Ar-H), 7.52 (t, *J* 8.2, 1H, Ar-H), 7.23 (d, *J* 8.2 2H, Ar-H), 2.67 (t, *J* 7.7, 4H, pyrimidine-CH_2), 1.69–1.29 (m, 24H, CH_2), 0.89 (t, *J* 6.4, 6H, CH_3); *m/z* (70 eV) (%) 698 (M^+, 45%), 295 (100).

1,3-Phenylene bis[4-(4-octyloxyphenylethynyl)benzoate] 1ToO8. Synthesized from 1,3-dihydroxybenzene (0.07 g, 0.64 mmol), 4-(4-octyloxyphenylethynyl)benzoic acid (0.48 g, 1.37 mmol). Yield 0.17g (34.3%); mp 154 °C (Found: C, 80.40; H, 7.02%; $C_{52}H_{54}O_6$ requires C, 80.62; H, 6.98%); δ_H($CDCl_3$; 200 MHz) 8.16 (d, *J* 8.6, 4H, Ar-H), 7.62 (d, *J* 8.6, 4H, Ar-H), 7.51–7.47 (d, 5H, Ar-H), 7.21–7.17 (d, 3H, Ar-H), 6.89 (d, *J* 8.8, 4H, Ar-H), 3.99 (t, *J* 6.5, 4H, OCH_2), 1.80–1.30 (m, 24H, CH_2), 0.90 (t, *J* 6.5, 6H, CH_3).

2-Methyl-1,3-phenylene bis[4-(5-octylpyrimidin-2-yl)benzoate] 2Py8. Synthesized from 2-methyl-1,3-dihydroxybenzene (0.11 g, 0.9 mmol) and **Py8** (0.55 g, 1.8 mmol). Yield 0.3 g (46.8%); mp 166 °C (Found: C, 75.86; H, 7.12; N, 7.59%;

$C_{45}H_{52}N_4O_4$ requires C, 75.84; H, 7.30; N, 7.87%); *m/z* (70 eV) 712 (M^+, 40%), 295 (100), 267 (8), 168 (8).

2-Nitro-1,3-phenylene bis[4-(5-hexylpyrimidin-2-yl)benzoate] 3Py6. Synthesized from 2-nitro-1,3-dihydroxybenzene (0.14 g, 0.9 mmol) and **Py6** (0.5 g, 1.8 mmol). Yield 0.18 g (29.1%); mp 145 °C (Found: C, 69.92; H, 5.96; N, 9.93%; $C_{40}H_{41}N_5O_6$ requires C, 69.87; H, 5.97; N, 10.19%); δ_H($CDCl_3$; 200 MHz) 8.69 (s, 4H, pyrimidine-H), 8.58 (d, *J* 8.8, 4H, Ar-H), 8.27 (d, *J* 8.8, 4H, Ar-H), 7.63 (t, 1H, Ar-H), 7.47 (d, 2H, Ar-H), 2.67 (t, 4H, pyrimidine-CH_2), 1.80–1.20 (m, 16 H, CH_2), 0.90 (t, 6H, CH_3); *m/z* (70 eV) 687 (M^+, 25%), 267 (100), 239 (7) 168 (8).

2-Nitro-1,3-phenylene bis[4-(5-octylpyrimidin-2-yl)benzoate] 3Py8. Synthesized from 2-nitro-1,3-dihydroxybenzene (0.09 g, 0.58 mmol) and **Py8** (0.35 g, 1.12 mmol). Yield 0.15 g (34.9%); mp 106 °C (Found: C, 71.01; H, 6.75; N, 9.08%; $C_{44}H_{49}N_5O_6$ requires C, 71.06; H, 6.59; N, 9.42%); δ_H($CDCl_3$; 200 MHz) 8.68 (s, 4H, pyrimidine-H), 8.58 (d, *J* 8.8, 4H, Ar-H), 8.26 (d, *J* 8.8, 4H, Ar-H), 7.70 (t, 1H, Ar-H), 7.47 (d, 2H, Ar-H), 2.65 (t, 4H, pyrimidine-CH_2), 1.80–1.20 (m, 24H, CH_2), 0.89 (t, 6H, CH_3); *m/z* (70 eV) 743 (M^+, 19%), 295 (100), 267 (7).

Naphthalene-2,7-diyl bis[4-(5-hexylpyrimidin-2-yl)benzoate] 4Py6. Synthesized from 2,7-dihydroxynaphthalene (0.15 g, 0.9 mmol) and **Py6** (0.5 g, 1.8 mmol). Yield 0.18 g (29.6%); mp 214–215 °C (Found: C, 76.21; H, 6.53; N, 8.11%; $C_{44}H_{44}N_4O_4$ requires C, 76.30; H, 6.36; N, 8.09%); δ_H($CDCl_3$; 400 MHz) 8.73 (s, 4H, pyrimidine-H), 8.63 (d, *J* 8.6, 4H, Ar-H), 8.37 (d, *J* 8.6, 4H, Ar-H), 7.94 (d, *J* 9.2, 2H, Ar-H), 7.72 (d, *J* 2.2, 2H, Ar-H), 7.39 (d, *J* 9.2, 2H, Ar-H), 2.68 (t, *J* 7.7, 4H, CH_2), 1.68 (t, *J* 7.3, 4H, CH_2), 1.4–1.3 (m, 12H, CH_2), 0.89 (t, *J* 7.0, 6H, CH_3).

***m*-Terphenyl-4,4″-diyl bis[4-(4-hexyloxyphenyl)benzoate] 5BpO6.** Synthesized from **5OH** (0.24g, 0.9 mmol) and 4-(4-hexyloxyphenyl)benzoic acid (0.6 g, 2.0 mmol). Yield 10 mg (1.4%); transitions (°C): Cr 258 M 268 Iso; δ_H($CDCl_3$; 200 MHz) 8.28 (d, 4H, *J* 8.6 Ar-H), 7.80 (s, 1H, Ar-H), 7.72 (d, *J* 7.6, 4H, Ar-H), 7.64–7.59 (m, 3H, Ar-H), 7.35 (d, *J* 8.6 4H, Ar-H), 7.28 (m, 8H, Ar-H), 7.00 (d, 4H, *J* 9.0, Ar-H), 4.03 (t, 4H, OCH_2), 1.81 (t, 4H, CH_2), 1.39–1.26 (m, 12H, CH_2), 0.93 (t, 6H, CH_3); *m/z* (70 eV) 281 (100%), 197 (15), 169 (10), 141 (5).

Pyridine-2,6-diylbis(1,4-phenylene) bis[4-(4-hexyloxyphenyl)-benzoate] 6BpO6. Synthesized from **6OH** (0.24 g, 0.9 mmol) and 4-(4-hexyloxyphenyl)carboxylic acid (0.60 g, 2.0 mmol). Yield 5 mg (0.7%); mp 267–268 °C; δ_H($CDCl_3$; 200 MHz) 8.28–8.20 (t, 6H, Ar-H), 7.71–7.35 (m, 17H, Ar-H), 7.00 (d, *J* 8.8, 4H, Ar-H), 4.01 (t, *J* 6.4, 4H, OCH_2), 1.81 (m, 4H, CH_2), 1.34–1.24 (m, 12H, CH_2), 0.90 (t, 6H, CH_3).

***m*-Terphenyl-4,4″-diyl bis[4-(4-*n*-octyloxyphenyliminomethyl)benzoate] 5ShO8.** Synthesized from **5OH** (0.24 g, 0.9 mmol) and 4-(4-*n*-octyloxyphenyliminomethyl)benzoic acid (0.71 g, 2.0 mmol). Yield 0.09 g (10.8%); mp >270 °C (decomp.) (Found: C, 79.66; H, 6.77; N, 3.31%; $C_{62}H_{64}N_2O_6$ requires C, 79.83; H, 6.87; N, 3.00%); *m/z* (70 eV) 932 (M^+, 4%), 597 (2), 484 (2), 352 (3), 336 (100), 241 (6), 224 (6), 195 (13).

***m*-Terphenyl-4,4″-diyl bis(4-*n*-butylbenzoate) 5Ph4.** Synthesized from **5OH** (0.24 g, 0.9 mmol) and 4-butylbenzoic acid (0.36 g, 2.0 mmol). Yield 0.17 g (32.5%); mp 134–135 °C (Found: C, 82.71; H, 6.59%; $C_{40}H_{38}O_4$ requires C, 82.47; H, 6.53%); δ_H($CDCl_3$; 400 MHz) 8.14 (2d, *J* 8.2, 4H, Ar-H), 7.80 (d, *J* 1.75, 1H, Ar-H), 7.70 (2d, *J* 8.6, 4H, Ar-H), 7.60–7.50 (m, 3H, Ar-H), 7.35–7.30 (m, 8H, Ar-H), 2.72 (t, *J* 7.7, 4H, CH_2), 1.69–1.36 (m, 8H, CH_2), 0.95 (t, *J* 7.4, 6H, CH_3).

***m*-Terphenyl-4,4″-diyl bis(4-hexylbenzoate) 5Ph6.** Synthesized from **5OH** (0.24 g, 0.9 mmol) and 4-hexylbenzoic acid (0.41 g, 2.0 mmol). Yield 0.19 g (33.1%); mp 105–106 °C (Found: C, 82.76; H, 7.32%; $C_{44}H_{46}O_4$ requires C, 82.76; H, 7.21%); δ_H($CDCl_3$; 200 MHz) 8.12 (d, *J* 8.2, 4H, Ar-H), 7.78 (d, *J* 1.4, 1H, Ar-H), 7.67 (2d, *J* 8.6, 4H, Ar-H), 7.58–7.51 (m, 3H, Ar-H), 7.33–7.27 (m, 8H, Ar-H), 2.69 (t, *J* 7.8, 4H, CH_2), 1.65–1.61 (m, 4H, CH_2), 1.32–1.24 (m, 12H, CH_2), 0.88 (t, *J* 6.6, 6H, CH_3).

***m*-Terphenyl-4,4″-diyl bis(4-dodecylbenzoate) 5Ph12** Synthesized from **5OH** (0.24 g, 0.9 mmol) and 4-dodecylbenzoic acid (0.58 g, 2.0 mmol). Yield 0.18 g (24.8%); mp 102–103 °C (Found: C, 83.47; H, 8.60%; $C_{56}H_{70}O_4$ requires C, 83.37; H, 8.68%); δ_H($CDCl_3$; 200 MHz) 8.15 (d, *J* 8.2, 4H, Ar-H), 7.81 (s, 1H, Ar-H), 7.70 (d, *J* 8.8, 4H, Ar-H), 7.61–7.54 (m, 3H, Ar-H), 7.36–7.30 (m, 8H, Ar-H), 2.72 (t, *J* 7.6, 4H, CH_2), 1.67–1.32 (m, 40H, CH_2), 0.89 (t, *J* 6.4, 6H, CH_3).

***m*-Terphenyl-4,4″-diyl bis(4-nonyloxybenzoate) 5PhO9.** Synthesized from **5OH** (0.24 g, 0.9 mmol) and 4-nonyloxybenzoic acid (0.53 g, 2.0 mmol). Yield 0.19 g (28.0%); mp 125–126 °C (Found: C, 79.59; H, 7.70%; $C_{50}H_{58}O_6$ requires C, 79.58; H, 7.69%); δ_H($CDCl_3$; 200 MHz) 8.18 (d, *J* 9.0, 4H, Ar-H), 7.81 (s, 1H, Ar-H), 7.70 (d, *J* 8.8, 4H, Ar-H), 7.60–7.53 (m, 3H, Ar-H), 7.32 (d, *J* 8.8, 4H, Ar-H), 7.00 (d, *J* 9.0, 4H, Ar-H), 4.06 (t, *J* 6.5, 4H, OCH_2), 1.87–1.77 (m, 4H, CH_2), 1.29–1.26 (m, 24H, CH_2), 0.90 (t, *J* 6.6, 6H, CH_3).

***m*-Terphenyl-4,4″-diyl bis(*trans*-4-octylcyclohexanecarboxylate) 5Cy8.** Synthesized from **5OH** (0.24 g, 0.9 mmol) and *trans*-4-octylcyclohexanecarboxylic acid (0.48 g, 2.0 mmol). Yield 0.89g (76.5%); mp 167–168 °C (Found: C, 81.77; H, 9.01%; $C_{48}H_{66}O_4$ requires C, 81.59; H, 9.35%); δ_H($CDCl_3$; 400 MHz) 7.73 (s, 1H, Ar-H), 7.62 (d, *J* 8.6, 4H, Ar-H), 7.55–7.51 (m, 3H, Ar-H), 7.16 (d, *J* 8.6, 4H, Ar-H), 2.50 (m, 2H, CH), 2.17–2.14 (m, 4H, CH_2), 1.90–1.87 (m, 4H, CH_2), 1.60–1.55 (m, 20H, CH_2), 1.26–0.95 (m, 18H, CH_2), 0.89 (t, *J* 6.8, 6H, CH_3).

***m*-Terphenyl-4,4″-diyl bis[4-(5-butylpyrimidin-2-yl)benzoate] 5Py4.** Synthesized from **5OH** (0.24 g, 0.9 mmol) and **Py4** (0.51 g, 2.0 mmol). Yield 0.2 g (30.1%); transition temperatures (°C): Cr 195 $S_{intercal}$ 203 Iso (Found: C, 78.16; H, 5.78; N, 7.73%; $C_{48}H_{42}N_4O_4$ requires C, 78.03; H, 5.73; N, 7.58%); δ_H($CDCl_3$; 200 MHz) 8.68 (s, 4H, pyrimidine-H), 8.57 (d, *J* 8.6, 4H, Ar-H), 8.32 (d, *J* 8.6, 4H, Ar-H), 7.81 (s, 1H, Ar-H), 7.70 (d, *J* 8.6, 4H, Ar-H), 7.60–7.5 (m, 3H, Ar-H), 7.34 (d, *J* 8.6, Ar-H), 2.66 (t, *J* 7.5, 4H, pyrimidine-CH_2), 1.70–1.19 (m, 8H, CH_2), 0.95 (t, *J* 7.2, 6H, CH_3); *m/z* (70 eV) 738 (M^+, 56%), 239 (100), 211 (10).

***m*-Terphenyl-4,4″-diyl bis[4-(5-hexylpyrimidin-2-yl)benzoate] 5Py6.** Synthesized from **5OH** (0.5 g, 1.8 mmol) and **Py6** (0.24 g, 0.9 mmol). Yield 0.23 g (32.2%); transitions (°C): Cr 209 $S_{intercal}$ 222 Iso (Found: C, 78.29; H, 6.50; N, 6.93%; $C_{52}H_{50}N_4O_4$ requires C, 78.56; H, 6.34; N, 7.05%); δ_H($CDCl_3$; 200 MHz) 8.67 (s, 4H, pyrimidine-H), 8.57 (d, *J* 8.4, 4H, Ar-H), 8.32 (d, *J* 8.4, 4H, Ar-H), 7.81 (s, 1H, Ar-H), 7.70 (d, *J* 8.4, 4H, Ar-H), 7.57–7.55 (m, 3H, Ar-H), 7.34 (d, *J* 8.4, 4H, Ar-H), 2.65 (t, *J* 7.8, 4H, pyrimidine-CH_2), 1.67–1.33 (m, 16H, CH_2), 0.89 (d, *J* 6.4, 6H, CH_3); *m/z* (70 eV) 794 (M^+, 82%), 267 (100), 239 (7).

***m*-Terphenyl-4,4″-diyl bis[4-(5-octylpyrimidin-2-yl)benzoate] 5Py8.** Synthesized from **5OH** (0.62 g, 2.0 mmol) and **Py8** (0.24 g, 0.9 mmol). Yield 0.36 g (47.1%); transitions (°C): Cr_1

105 Cr_2 178 $S_{intercal}$ 206 Iso (Found: C, 80.14; H, 6.64; N, 6.75%; $C_{56}H_{58}N_4O_4$ requires C, 79.03; H, 6.87; N, 6.58%); δ_H($CDCl_3$; 200 MHz) 8.70 (s, 4H, pyrimidine-H), 8.59 (d, *J* 8.6, 4H, Ar-H), 8.34 (d, *J* 8.6, Ar-H), 7.83 (s, 1H, Ar-H), 7.73 (d, *J* 8.6, 4H, Ar-H), 7.65–7.55 (m, 3H, Ar-H), 7.36 (d, *J* 8.6, 4H, Ar-H), 2.68 (d, *J* 7.6, 4H, pyrimidine-CH_2), 1.69–1.28 (m, 24H, CH_2), 0.89 (d, *J* 6.5, 6H, CH_3); *m*/*z* (70 eV) 858 (M^+, 38%), 295 (100), 267 (7), 239 (43).

Pyridine-2,6-diylbis(1,4-phenylene) bis[4-(5-hexylpyrimidin-2-yl)benzoate] 6Py6. Synthesized from **6OH** (0.24 g, 0.9 mmol) and **Py6** (0.5 g, 1.8 mmol). Yield 0.3 g (41.9%), transitions (°C): Cr 224 B1 242 Iso (Found: C, 77.12; H, 6.53; N, 8.63%; $C_{51}H_{49}N_5O_4$ requires C, 76.96; H, 6.21; N, 8.80%); δ_H($CDCl_3$; 200 MHz) 8.68 (s, 4H, pyrimidine-H), 8.58 (d, *J* 8.6, 4H, Ar-H), 8.33 (d, *J* 8.6, 4H, Ar-H), 8.23 (d, *J* 8.6, 4H, Ar-H), 7.88–7.69 (m, 3H, Py-H), 7.38 (d, *J* 8.6, 4H, Ar-H), 2.65 (t, *J* 7.5, 4H, pyrimidine-CH_2), 1.67–1.24 (m, 16H, CH_2), 0.89 (t, *J* 6.6, 6H, CH_3); *m*/*z* (70 eV) 795 (M^+, 88%), 267 (100), 239 (8).

Pyridine-2,6-diylbis(1,4-phenylene) bis[4-(5-octylpyrimidin-2-yl)benzoate] 6Py8. Synthesized from **6OH** (0.24 g, 0.9 mmol), **Py8** (0.62 g, 2.0 mmol). Yield 0.37 g (48.4%); transitions (°C): Cr_1 131 Cr_2 204 Cr_3 231 (B1 230) Iso; δ_H($CDCl_3$; 200 MHz) 8.68 (s, 4H, pyrimidine-H), 8.58 (d, *J* 8.6, 4H, Ar-H), 8.33 (d, *J* 8.6, 4H, Ar-H), 8.23 (d, *J* 8.6, 4H, Ar-H), 7.88–7.69 (m, 3H, Py-H), 7.38 (d, *J* 8.6, 4H, Ar-H), 2.65 (t, *J* 7.5, 4H, pyrimidine-CH_2), 1.66–1.27 (m, 24H, CH_2), 0.87 (t, *J* 6.4, 6H, CH_3); *m*/*z* (70 eV) 851 (M^+, 85%), 295 (100), 267 (10).

***m*-Terphenyl-4,4″-diyl bis[4-(4-octylbenzoyloxy)benzoate] 5Bz8.** Synthesized from **5OH** (0.24 g, 0.9 mmol) and 4-(4-octylbenzoyloxy)benzoic acid (0.71 g, 2.0 mmol). Yield 0.25 g (29.8%); transitions (°C): Cr_1 173 Cr_2 180 B1 207 Iso; δ_H($CDCl_3$; 200 MHz) 8.30 (d, *J* 8.6, 4H, Ar-H), 8.10 (d, *J* 8.6, 4H, Ar-H), 7.80 (s, 1H, Ar-H), 7.70 (d, *J* 8.6, 4H, Ar-H), 7.60–7.53 (m, 3H, Ar-H), 7.40–7.30 (m, 12H, Ar-H), 2.70 (t, *J* 7.6, 4H, Ar-CH_2), 1.65–1.26 (m, 24H, CH_2), 0.87 (t, *J* 6.4, 6H, CH_3).

***m*-Terphenyl-4,4″-diyl bis[4-(4-octyloxybenzoyloxy)benzoate] 5BzO8.** Synthesized from **5OH** (0.15 g, 0.56 mmol), 4-(4-octyloxybenzoyloxy)benzoic acid (0.39 g, 1.1 mmol). Yield 0.12 g (21.8%), transitions (°C): Cr 160 B1 226 Iso (Found: C, 77.22; H, 6.65%; $C_{62}H_{62}O_{10}$ requires C, 77.02; H, 6.42%); δ_H($CDCl_3$; 200 MHz) 8.29 (d, *J* 8.6, 4H, Ar-H), 8.14 (d, *J* 9.0, 4H, Ar-H), 7.80 (s, 1H, Ar-H), 7.70 (d, *J* 8.6, 4H, Ar-H), 7.56–7.54 (m, 3H, Ar-H), 7.40–7.30 (m, 8H, Ar-H), 6.97 (d, *J* 9.0, 4H, Ar-H), 4.04 (t, *J* 6.5, 4H, OCH_2), 1.85–1.29 (m, 14H, CH_2), 0.88 (t, *J* 6.5, 6H, CH_3).

***m*-Terphenyl-4,4″-diyl bis[4-(4-nonyloxybenzoyloxy)benzoate] 5BzO9.** Synthesized from **5OH** (0.24 g, 0.9 mmol), 4-(4-nonyloxybenzoyloxy)benzoic acid (0.77 g, 2.0 mmol). Yield 0.38 g (42.5%); transitions (°C): Cr 161 B1 219 Iso (Found: C, 77.18; H, 6.94; $C_{64}H_{66}O_{10}$ requires C, 77.24; H, 6.68%); δ_H($CDCl_3$; 200 MHz) 8.32 (d, *J* 8.8, 4H, Ar-H), 8.17 (d, *J* 8.9, 4H, Ar-H), 7.82 (s, 1H, Ar-H), 7.72 (d, *J* 8.8, 4H, Ar-H), 7.62–7.43 (m, 3H, Ar-H), 7.42–7.27 (m, 12H, Ar-H), 7.01 (d, *J* 8.9, 4H, Ar-H), 4.07 (t, *J* 6.5, 4H, OCH_2), 1.87–1.25 (m, 28H, CH_2), 0.9 (t, *J* 6.4, 6H, CH_3); *m*/*z* (70 eV) 994 (M^+, 8%), 367 (4), 247 (100), 121 (76).

Pyridine-2,6-diylbis(1,4-phenylene) bis[4-(4-nonyloxybenzoyloxy)benzoate] 6BzO9. Synthesized from **6OH** (0.24 g, 0.9 mmol) and 4-(4-nonyloxybenzoyloxy)benzoic acid (0.77 g, 2.0 mmol). Yield 0.35 g (39.1%); transitions (°C): Cr 179 B1 246 Iso (Found: C, 76.13; H, 6.76; N, 1.28%; $C_{63}H_{65}NO_{10}$ requires C, 75.96; H, 6.58; N, 1.41%); δ_H($CDCl_3$; 200 MHz) 8.35–8.15 (m, 12H, Ar-H), 7.74 (m, 3H, Py-H), 7.42–7.36 (m, 8H, Ar-H), 7.0 (d, 4H, *J* 9.0, Ar-H), 4.07 (t, 4H, *J* 6.4, OCH_2), 1.82 (m, 4H, CH_2), 1.3 (m, 24H, CH_2), 0.87 (t, *J* 6.6, 6H, CH_3).

2′-Nitro-*m*-terphenyl-4,4″-diyl bis[4-(4-nonyloxybenzoyloxy)benzoate] 7BzO9. Synthesized from **7OH** (0.28 g, 0.9 mmol) and 4-(4-nonyloxybenzoyloxy)benzoic acid (0.77 g, 2.0 mmol). Yield 35 mg (3.7%); transitions (°C): Cr_1 108 Cr_2 149 B1 197 N 217 Iso (Found: C, 74.20; H, 6.49; N, 1.26%; $C_{64}H_{65}NO_{12}$ requires C, 73.92; H, 6.26; N, 1.35%); δ_H($CDCl_3$; 200 MHz) 8.29 (d, 4H, *J* 8.6, Ar-H), 8.16 (d, *J* 9.0, 4H, Ar-H), 7.63–7.28 (m, 15H, Ar-H), 7.0 (d, *J* 9.0, 4H, Ar-H), 4.07 (t, *J* 6.5, 4H, OCH_2), 1.82 (m, 4H, CH_2), 1.3 (m, 24H, CH_2), 0.9 (m, 6H, CH_3).

1,3-Bis{4-[4-(4-nonyloxybenzoyloxy)benzoyloxy]-phenylethynyl}benzene 8BzO9. Synthesized from **8OH** (0.31 g, 1.0 mmol) and 4-(4-nonyloxybenzoyloxy)benzoic acid (0.77 g, 2.0 mmol). Yield 0.38 g (36.5%); transitions (°C): Cr_1 92 Cr_2 159 B1 239 Iso (Found: C, 78.00; H, 6.58%; $C_{68}H_{66}O_{10}$ requires C, 78.29; H, 6.38%); δ_H ($CDCl_3$; 200 MHz) 8.26 (d, *J* 8.8, 4H, Ar-H), 8.14 (d, *J* 9.0, 4H, Ar-H), 7.72 (s, 1H, Ar-H), 7.59 (d, *J* 8.8, 4H, Ar-H), 7.59 (d, *J* 8.6, 2H, Ar-H), 7.39–7.27 (m, 5H, Ar-H), 7.23 (d, *J* 8.6, 4H, Ar-H), 6.97 (d, *J* 9.0, 4H, Ar-H), 4.04 (t, *J* 6.5, 4H, OCH_2), 1.81 (t, *J* 6.9, 4H, CH_2), 1.27–1.24 (m, 24 H, CH_2), 0.87 (t, *J* 6.8, 6H, CH_3); *m*/*z* (70 eV) 1042 (M^+, 5%), 367 (9), 247 (100), 121 (51).

1,3-Bis{4-[4-(5-octylpyrimidin-2-yl)benzoyloxy]phenylethynyl}benzene 8Py8. Synthesized from **8OH** (0.31 g, 1.0 mmol) and **Py8** (0.62 g, 2.0 mmol). Yield 0.27 g (30.1%); transitions (°C): Cr_1 126 Cr_2 204 $S_{intercal}$ 236 Iso (Found: C, 80.01; H, 6.60; N, 6.01%; $C_{60}H_{58}N_4O_4$ requires C, 80.15; H, 6.50; N, 6.23%); δ_H($CDCl_3$; 200 MHz) 8.69 (s, 4H, pyrimidine-H), 8.59 (d, *J* 8.4, 4H, Ar-H), 8.32 (d, *J* 8.4, 4H, Ar-H), 7.72 (s, 1H, Py-H), 7.60 (d, *J* 8.6, 4H, Ar-H), 7.50 (d, *J* 7.4, 2H, Ar-H), 7.38–7.21 (m, 5H, Ar-H), 2.65 (t, *J* 7.6, 4H, CH_2), 1.66–1.26 (m, 24H, CH_2), 0.87 (t, *J* 6.6, 6H, CH_3); *m*/*z* (70 eV) 898 (M^+, 42%), 295 (100).

1,3-Bis[4-(4-octylbenzoyloxy)phenylethynyl]benzene 8Ph8. Synthesized from **8OH** (0.31 g, 1.0 mmol) and 4-octylbenzoic acid (0.47 g, 2.0 mmol). Yield 0.25 g (37.4%); mp 127 °C (Found: C, 84.52; H, 7.42; $C_{52}H_{54}O_4$ requires C, 84.06; H, 7.33%); δ_H ($CDCl_3$; 400 MHz) 8.09 (2d, *J* 8.4, 4H, Ar-H), 7.71 (s, 1H, Ar-H), 7.57 (2d, *J* 8.8, 4H, Ar-H), 7.50–7.47 (m, 2H, Ar-H), 7.35–7.39 (m, 5H, Ar-H), 7.22–7.18 (m, 4H, Ar-H), 2.68 (t, *J* 7.7, 4H, CH_2), 1.64 (t, *J* 7.0, 4H, CH_2), 1.30–1.26 (m, 20H, CH_2), 0.87 (t, *J* 6.8, 6H, CH_3); *m*/*z* (70 eV) 742 (M^+, 2%), 217 (100), 91 (14).

1-{4-[4-(4-Nonyloxybenzoyloxy)benzoyloxy]phenyl}-3-{4-[4-(4-nonyloxybenzoyloxy)benzoyloxy]phenylethynyl}benzene 9BzO9. Synthesized from **9OH** (0.26 g, 0.9 mmol) and 4-(4-nonyloxybenzoyloxy)benzoic acid (0.77 g, 2.0 mmol). Yield 0.20 g (21.8%); transitions (°C): Cr_1 111 Cr_2 142 B1 231 Iso (Found: C, 77.61; H, 6.67%; $C_{66}H_{66}O_{10}$ requires C, 77.77; H, 6.53%); δ_H($CDCl_3$; 200 MHz): 8.32–8.24 (m, 4H, Ar-H), 8.14 (d, *J* 9.0, 4H, Ar-H), 7.77 (s, 1H, Ar-H), 7.68–7.21 (m, 15H, Ar-H), 6.97 (d, *J* 8.8, 4H, Ar-H), 4.04 (t, *J* 6.5, 4H, OCH_2), 1.85–1.24 (m, 28H, CH_2), 0.87 (t, *J* 6.3, 6H, CH_3).

1-{4-[4-(5-Octylpyrimidin-2-yl)benzoyloxy]phenyl}-3-{4-[4-(5-octylpyrimidin-2-yl)benzoyloxy]phenylethynyl}benzene 9Py8. Synthesized from **9OH** (0.26 g, 0.9 mmol) and **Py8** (0.62 g, 2.0 mmol). Yield 0.30 g (38.1%); transitions (°C): Cr 183 $S_{intercal}$ 220 Iso (Found: C, 79.79; H, 6.90; N, 6.23%; $C_{58}H_{58}N_4O_4$ requires C, 79.60; H, 6.68; N, 6.40%); δ_H($CDCl_3$;

400 MHz) 8.67 (d, *J* 1.4, 4H, pyrimidine-H), 8.56 (2t, 4H, Ar-H), 8.31 (m, 4H, Ar-H), 7.78 (s, 1H, Ar-H), 7.67–7.25 (m, 11H, Ar-H), 2.64 (t, *J* 7.6, 4H, CH_2), 1.70–1.63 (m, 4H, CH_2), 1.50–1.26 (m, 20H, CH_2), 0.86 (t, *J* 6.8, 6H CH_3).

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