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Synthesis and study of new rod-like mesogens containing 2-aminothiophene unit

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ABSTRACT

We present a synthesis and mesomorphic properties of a new series of rod-like mesogens. All the compounds possess a substituted 2-aminothiophene unit as a main element in the structure attached to a stilbene moiety with a terminal alkyloxy chain (OR^1, OR^2 where $R^1=C_nH_{2n+1}$, $R^2=C_mH_{2m+1}$; n, m ranging from 6 to 12). The synthesis of alkyloxybiphenyl substituted 2-aminothiophenes was carried out by the Gewald reaction and the appropriate reaction conditions were investigated. The liquid–crystalline properties were studied via polarizing optical microscopy, differential scanning calorimetry and X-ray diffraction. These materials exhibit nematic and/or smectic A phases. The influence of structural changes (variation in alkyloxy chain length and symmetry of the molecule) on mesogenic behaviour is discussed. Evaluation of UV–vis, fluorescent and electrochemical properties are also included.

1. Introduction

The area of liquid crystals (LCs) arguably belongs to the one of the most extensive and dynamic fields of present-day materials research. The first observations on compounds possessing mesogenic phase behaviour are dated 150 years ago[1] and are related to scientific works of Planer,[2] Reinitzer[3] and Lehmann.[4] Liquid crystals combine order and mobility and form well-organized supramolecular assemblies that exhibit a variety of physical properties, which makes them attractive for utilization in the fields of nanoscience.[5–7] Since 1989, when Hitachi Ltd. presented the first type of LCD (low-power flat-panel liquid–crystal display),[8] liquid crystals became essential materials of the modern era. Important for display applications are thermotropic liquid crystals, which change phase with temperature. They usually represent classical rod-like molecules built up from the aromatic rigid core with one or two alkyl terminal chains possessing mainly nematic and/or smectic phase.[9]

Nowadays, the increasing scientific interest is focused on the prediction and monitoring of the properties of the liquid crystals at a nanoscale level. As an effective way much work has been done on molecular design and synthesis leading to well-defined supramolecules. The key criteria among such design processes are the yields achievable in each synthetic step and the nature of the terminal groups. The induction of liquid crystallinity in π-conjugated materials is one of the promising approaches to control the molecular self-organization processes and can lead to the development of new electro- and photofunctional metamaterials.[10] The versatility of thiophene chemistry and the π-donating character of the thiophene moiety (electronic affinity: $EA=-1.17$ eV, ionization potential: $IP=8.87$ eV) provides the basis for the synthesis of most conjugated π-systems with a high degree of functionalization.[11] Generally, thiophene containing compounds having donor–acceptor character are known as active components in organic electronic devices and optoelectronics.[12] Several examples show, that liquid crystals containing a thiophene moiety in the structure exhibit, besides thermotropic behaviour, also interesting photoconductive,[13] fluorescent[14] and charge-transfer properties.[15]

We report herein a rapid and simple synthesis of model rod-like mesogens with the functionalized aminothiophene moiety as part of the central rigid core linked to a fluorescent stilbene segment with an alkyloxy tail on both ends. These compounds exhibit nematic and smectic A phases and show interesting fluorescent properties. Towards the synthesis of the 2-aminothiophene part in the designed compounds, the Gewald reaction was explored.[16] As we have shown previously, the free amino group allows its replacement in a manner usable for the preparation of thiophene-containing structures with the possibility to be integrated into polymers with tunable electronic and optical properties.[17] However, this approach has not been applied in a design and synthesis of liquid–crystals so far. The present synthesis and physical study can provide a new approach in the development of liquid–crystalline materials with a thiophene-based central unit.

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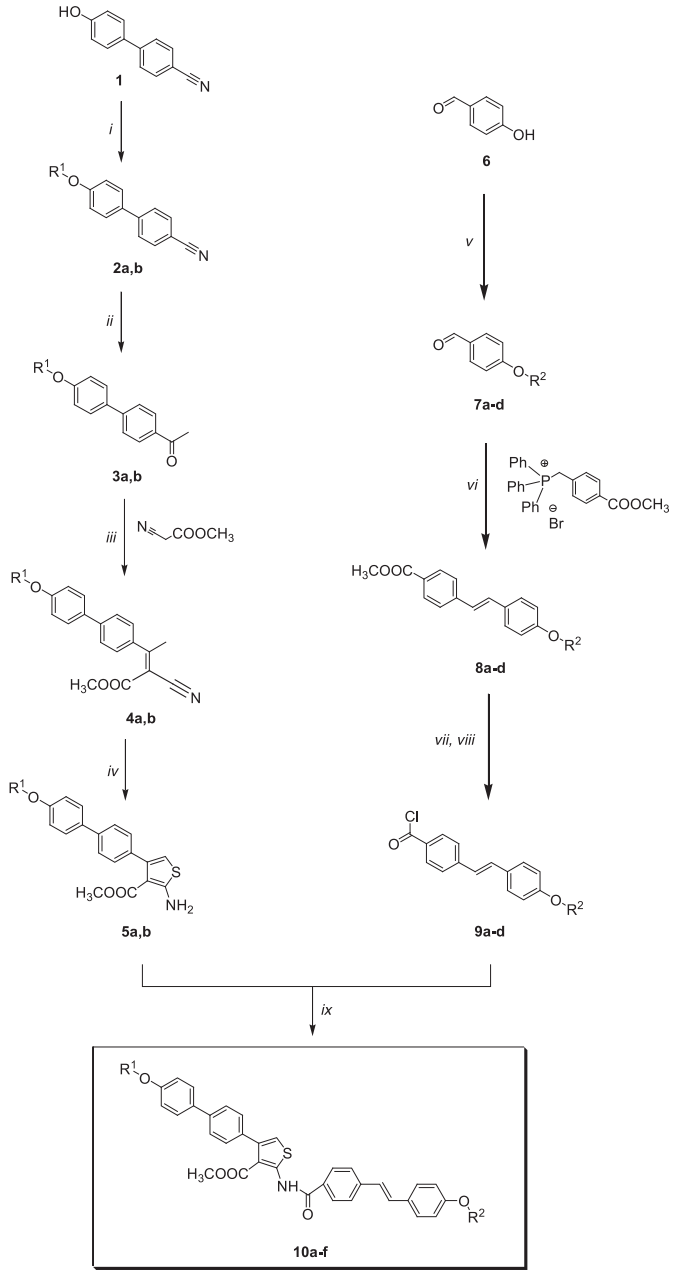
2. Results and discussion

2.1. Synthesis

The synthesis of target thiophene containing mesogens **10a**–**f** is described in Scheme 1. The 2-aminothiophene core in **5a** and **5b** was formed via a four step reaction sequence. The hydroxy group in 4′-hydroxybiphenyl-4-carbonitrile (**1**) was initially reacted with a halogenated alkane, 1-bromohexane or 1-bromooctane, respectively, using potassium carbonate in DMF. Under these conditions the corresponding 4′-(alkyloxy)-biphenyl-4-carbonitriles (**2a**,**b**) were isolated.[18] The carbonyl group was introduced in a second step with methylmagnesium iodide prepared in situ under Grignard reaction conditions. Formed ketones **3a**,**b** with a scrambled alkyloxyl tail represent an *CH*-active oxo-components suitable for the Gewald thiophene synthesis, which encompasses a Knoevenagel condensation and cyclization reaction sequence. The reaction conditions leading to a new type of substituted 2-aminothiophenes **5a** and **5b** were slightly modified and are described below (Scheme 2, Table 2).



Scheme1. Synthesis of thiophene-containing rod-like mesogens **10a**–**f**. Reagents and conditions: (i) alkylbromide (1.2 equiv), K_2CO_3 (2.0 equiv), DMF, 120 °C, 16 h; (ii) Mg (1.5 equiv), CH_3I (1.5 equiv), Et_2O, 36 °C, 6 h; (iii) Knoevenagel condensation: *see* Scheme 2 and Table 2; (iv) Gewald cyclization: see Scheme 2 and Table 2; (v) alkylbromide (1.2 equiv), K_2CO_3 (1.2 equiv), DMF, 80 °C, 8 h; (vi) Wittig salt (1.5 equiv), K_2CO_3 (2.0 equiv), 18-crown-6 (cat. amount), DCM/THF (1:1), reflux, 40 h; (vii) KOH aq (10.0 equiv), H_2O/EtOH (1:1), reflux, 5 h; (vii) oxalyl chloride (4.0 equiv), DCM, reflux 3 h; (ix) DMAP, TEA (cat. amount), toluene, reflux 12–24 h.

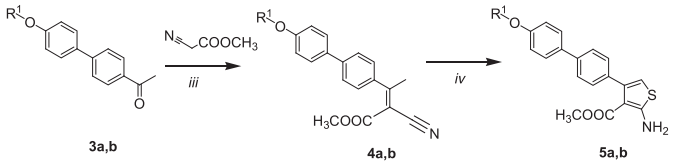
The four-step procedure was employed for the synthesis of the stilbene part **9a**–**d** (Scheme 1). Treatment of 4-hydroxybenzaldehyde (**6**) with corresponding alkylbromide in DMF using potassium carbonate led to 4-alkyloxy-benzaldehydes **7a**–**d**.[19] Reaction of **7a**–**d** with Wittig salt in a dichloromethane–THF mixture in the presence of 18-crown-6 and potassium carbonate afforded 4-[2-(4-alkyloxy-biphenyl)-vinyl]-benzoic acid methyl esters **8a**–**d**.[20] The ester moiety was subsequently hydrolyzed with an aqueous solution of KOH in ethanol and the carboxylic acid salt obtained was converted into acyl chloride **9a**–**d** with oxalyl chloride in dichloromethane.[21] The described synthesis represents a convenient and easy route to 4-[2-(4-alkyloxy-phenyl)-vinyl]-benzoyl chlorides (**9a**–**d**) requiring only one purification step—the crystallization of methyl esters **8a**–**d** after the Wittig reaction.

The acyl chlorides **9a**–**d** were finally reacted with 2-aminothiophenes **5a** or **5b**, respectively, in boiling toluene using DMAP as nucleophilic catalyst to afford the final thiophene-containing mesogenic compounds (Scheme 1). Final products **10a**–**f** were isolated from the dark slurry in acceptable yields 35–45% (Table 1).

Table 1
Thiophene-containing rod-like mesogens **10a**–**f**

Compound	R^1(=C_nH_{2n+1})	R^2(=C_mH_{2m+1})	Yield (%)
10a	C_6H_{13}	C_6H_{13}	42%
10b	C_6H_{13}	C_8H_{16}	45%
10c	C_8H_{16}	C_6H_{13}	40%
10d	C_8H_{16}	C_8H_{16}	42%
10e	C_8H_{16}	$C_{10}H_{21}$	38%
10f	C_8H_{16}	$C_{12}H_{24}$	35%

The Gewald synthesis is probably the most versatile reaction for the preparation of highly substituted 2-aminothiophenes, where by choosing suitable substrates the functionalization of the final thiophene derivative is precisely predicted.[22] Our initial effort to synthesize 2-aminothiophenes **5a** and **5b** employing the simplest one-pot procedure resulted in complicated mixtures that were difficult to purify. Generally, the one-pot Gewald method has limited scope in the synthesis of 2-aminothiophenes with an unsubstituted α-position or provide products in very poor yields.[23] Accordingly, the two-step variation of the Gewald reaction was performed. The α,β-unsaturated nitriles (*so called* ylidenes or acrylonitriles) **4a** and **4b** were obtained via Knoevenagel condensation by heating the respective ketone **3a** or **3b** with methylcyanoacetate (2.0 equiv) in toluene at 80 °C using ammonium acetate as a promoter for the reaction. Because of the low reactivity of the starting ketones **3a**,**b**, NH_4OAc was used in equimolar amounts.[24] The use of Dean–Stark apparatus was replaced by trimethylsilylacetate as an organic desiccant (TMSOAc, in 1.5 equiv relative to ketone). Employment of TMSOAc also prevents the possible side-reaction—the self-condensation of the formed ylidene.[25] The conversion of starting compounds into condensation products never proceeded to completion even if the reaction time was extended to 12 h. The yields of ylidenes **4a**,**b** after isolation and purification from unreacted substrates were about 60% (Table 2). The ylidenes were subsequently reacted with sulfur (1.5 equiv)



Scheme 2. The Gewald synthesis of **5a**,**b**.

Table 2
Base and solvent screen for the Gewald reaction (Scheme 2)

Compound	Reaction conditions (reagents, temperature, time)	Yield (%)
Knoevenagel condensation (iii)		
4a	NH_4OAc (1.0 equiv), TMSOAc	58%
4b	(1.5 equiv), toluene, 80 °C, 12 h	61%
Cyclization (iv)		
5a	**A**: Et_3N (2.2 equiv), S_8 (2.0 equiv), Methanol, 45 °C, 12 h	28%
	B: Morpholine (2.2 equiv), S_8 (2.0 equiv), Methanol, 45 °C, 12 h	40%
	C: Morpholine (2.2 equiv), S_8 (2.0 equiv), Tetrahydrofuran, 50 °C, 12 h	60%
5b	**A**: Et_3N (2.2 equiv), S_8 (2.0 equiv), Methanol, 45 °C, 12 h	30%
	B: Morpholine (2.2 equiv), S_8 (2.0 equiv), Methanol, 45 °C, 8 h	39%
	C: Morpholine (2.5 equiv), S_8 (2.0 equiv), Tetrahydrofuran, 50 °C, 12 h	64%

under basic conditions to give the 2-aminothiophenes **5a**,**b** (Scheme 2).[26] In order to increase the yields and purity of the desired 2-aminothiophenes **5a**,**b** a brief solvent and base screen was investigated for the cyclization step. The reaction carried out in methanol at 45 °C with triethylamine (2.2 equiv)[27] gave the corresponding compounds **5a**,**b** in approximately 30% yield after 12 h (Table 2).

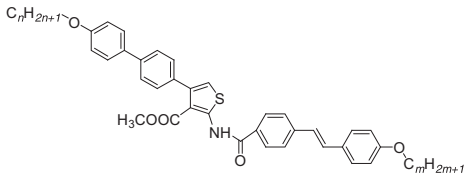
Neither extension of the reaction time or increasing the reaction temperature did not give better results. Using morpholine (2.2 equiv) as a base in methanol[28] showed an increase in product yield to 40% (Table 2). The highest reactivity was observed when the reaction was carried out in THF at 50 °C with morpholine (2.2 equiv). The products **5a** and **5b** were obtained in 60% and 64% yield, respectively, after 12 h (Table 2). Compounds **5a** and **5b** represent novel types of 2-aminothiophenes where the alkylbiphenyl substituent in the β-position is established during the synthetic procedure and no other modifications of the final structure are required.

2.2. Mesomorphic properties

Mesomorphic properties of compounds **10a**–**f** were investigated by polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray measurements. Phase types, their thermal stability, transition enthalpies and layer thickness in smectic A phase are given in Table 3. Chosen POM image of representative nematic phase and characteristic images from X-ray measurements are shown in Figs. 1 and 2.

All compounds **10a**–**f** display thermotropic liquid crystalline properties forming nematic and/or smectic A mesophases, which are determined by the length of the terminal alkyl groups and symmetry of the molecule. For compounds with total alkyl chain length (n+m) of 14 carbon atoms (**10b**, **c**) and of 16 carbon atoms

Table 3
Phase transitions, transition enthalpies and layer thickness in SmA phase of studied compounds



10a-f

Compound	n	m	Phase transition (°C), transition enthalpies (kJ mol^{-1})	Layer thickness in SmA (Å)
10a	6	6	Iso 229.8 (0.62) N 144.6 (40.94) Cr	—
10b	6	8	Iso 211.1 (0.70) N 161.7 (0.10) SmA 144.0 (36.40) Cr	40.0
10c	8	6	Iso 212.4 (0.40) N 163[a] SmA 130.3 (35.93) Cr	40.8
10d	8	8	Iso 221.5 (0.87) N 196.6 (0.37) SmA 124.9 (25.21) Cr	42.2
10e	8	10	Iso 150.66 (1.06) N 143.25 (5.65) Cr 108.3 (17.35)	—
10f	8	12	Iso 111.7 (0.25) N 96.7 (19.06) Cr	—

Abbreviations used: Cr=crystal, N=nematic, SmA=smectic A, Iso=isotropic.
[a] Value taken from X-ray measurements, not detectable on DSC.

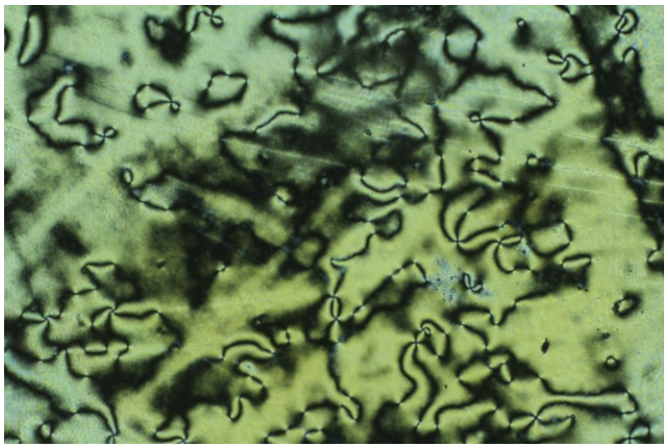


Fig. 1. Optical texture of a nematic phase of compound **10c** at 207 °C (on cooling).

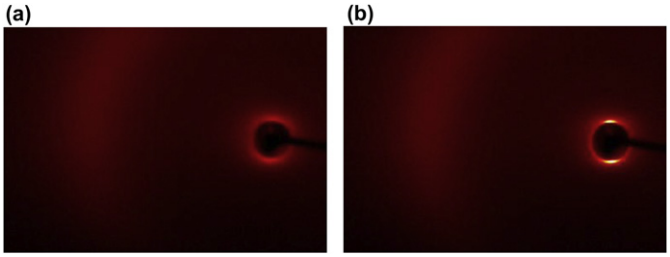


Fig. 2. X-ray diffraction patterns for compound **10c** in: (a) nematic phase at 187 °C and (b) smectic A phase at 158 °C.

(**10d**) nematic and smectic A phases are observed. Whereas for compounds **10a** (n+m=12), **10e** and **10f** (n+m=18 and 20, respectively) only a nematic phase is observed. Compounds **10b** and **10c**, with interchanged alkyl tails on both sides of the molecule

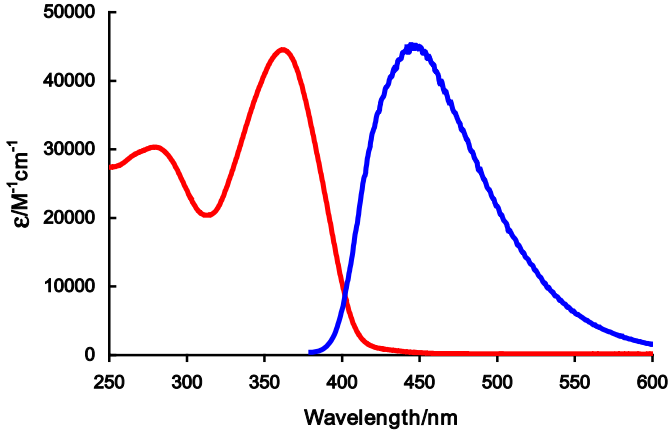
(n+m=14 carbon atoms), exhibit enantiotropic nematic and monotropic smectic A phase. The transition temperatures in SmA for **10b** with n=6, m=8 and for **10b** with n=8, m=6 are very close. For compound **10d**, with n+m=16 carbon atoms, where n=m=8, both enantiotropic nematic and enantiotropic smectic A phase are observed. The layer thickness in smectic A for **10b**–**d** is almost equal to the molecule length, therefore it can be assumed that layers are built from almost entirely stretched molecules and do not intercalate. This type of behaviour is typical for rod-like molecules built of an aromatic core with aliphatic tails. For less symmetric compounds **10e** and **10f**, when the number of alkyl chain is increased from m=8 to m=10, 12 (n+m=18 carbon atoms in **10e** and n+m=20 carbon atoms in **10f**), the formation of smectic A phase is completely suppressed and only the nematic phase is observed.

We can conclude, that in the series of presented mesogens **10a**–**f**, the compounds with medium sized alkyl chains and higher symmetry (**10b**, **10c** where n+m=14, n=6 or 8, m=6 or 8, **10d** with n+m=16, n=m=8) exhibit both, nematic and smectic A phase, while shortening of alkyl chains (**10a**, n+m=12, n=m=6) or elongation and symmetry breaking (**10e**, **10f**, n+m=18, 20) favours only the nematic phase.

Typical schlieren texture of nematic phase of **10c** compound is presented in Fig. 1. The X-ray data were collected for all synthesized mesogenic compounds. The X-ray pattern for nematic phase consists of two diffused signals related to the short range positional order along director (averaged long axes direction) and perpendicular to it (Fig. 2a). With lowering temperature the low angle signal narrows, showing increasing positional order in the system. In smectic A phases low angle signals become resolution limited (Fig. 2b).

2.3. UV–vis and fluorimetry

The spectroscopic properties of the compounds show very little dependence on the alkyl chain length. The absorption and fluorescence spectrum of **10c** as the representative for this group of compound is shown in Graph 1. All compounds exhibit two absorption peaks in the UV–vis region: with λ^1_{max}=280 nm (ε=3×10^4 M^{-1} cm^{-1}) and λ^2_{max}=363 nm (ε=4.5×10^4 M^{-1} cm^{-1}) and a single slightly asymmetric fluorescence signal with a maximum at 450 nm. The fluorescence quantum yield in solution for this compound **10c** was found to be ca. 6%. The fluorescence of compound is related to the presence of the stilbene unit in the molecular structure, the thiophene part is fluorescence inactive, as checked for the **5a** semiproduct. The fluorescence decay time is shorter for compound dissolved in organic solvent than in solid state (0.96 ns and 1.76 ns, respectively). This is opposite behaviour to usual, in which quenching of the fluorescence is much faster in the crystal phase because of strong interactions between molecules. However it should be noted that, for stilbene compounds in solution relaxation from the excited state involves twisting of the phenyl rings of the stilbene unit, while in solid state this relaxation channel is closed as the twisting of phenyl rings becomes frozen.[29] The optical band gap derived from the onset of absorption spectrum is equal 3.0 eV.



Graph 1. Absorption (red line) and fluorescence (blue line) spectra for **10c** dissolved in chloroform at 25 °C (c=3.2×10^{-5} mol dm^{-3}).

2.4. Electrochemistry

The electrochemical and electronic properties of compounds were investigated by means of cyclic voltammetry and differential pulse voltammetry. Resolution of cyclic voltammetry was too low to obtain the value of the first oxidation potential E_{ox} therefore we used differential pulse voltammetry and obtained E_{ox}≈1.47 V versus NHE and the first reduction potential E_{red}≈−1.56 V versus NHE. The measured electrochemical band gap is therefore almost equal with the value of the optical band gap. It should be mentioned that during cyclic voltammetry measurements we observed a gradual shift of the signals towards higher potentials in the positive potential range and a decrease in current intensity. At the same time on the surface of the carbon electrode a shiny blue film developed. This behaviour was not observed while measurements were performed in the negative potentials range. On this basis we conclude, that studied compounds are capable of electropolymerisation.

3. Conclusion

A convenient synthesis of 4-alkyloxy-biphenyl substituted 2-aminothiophenes was described. The final products were mesogenic materials. It was found that these compounds exhibit nematic and smectic A phases and mesomorphic behaviour is dependent on the length of the alkyloxy tails and on the symmetry of the molecule. The compounds with short terminal alkyloxy chains and less symmetric molecules with one prolonged alkyloxy chain favours only the formation of nematic phase. For symmetric compounds with middle sized terminal alkyloxy chains also smectic A phase occurs. Investigated compounds exhibit interesting fluorescence related to the presence of stilbene unit in the molecular structure. The electrochemical band gap for this material was found to be ca. 3.0 eV.

4. Experimental section

4.1. General

All chemicals were purchased from Sigma–Aldrich and used without further purification. All solvents were HPLC grade and used as supplied. Compositions of the synthesized compounds were determined by elemental analysis (FlashEA 1112, Thermo Finnigan). ESI-MS spectra were recorded on Mass Quattro LC. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Varian Unity Plus instrument at 25 °C. The measurements were done using protiated solvent $CDCl_3$ with TMS as the internal standard. Two dimensional spectra gs-H,H-COSY, 1D-gs-NOESY, gs-HSQC and gs-HMBC were measured using standard software programs provided by Varian. Coupling constants (J) are quoted to the nearest 0.1 Hz and chemical shifts (δ-scale) are quoted in parts per million (ppm). The following abbreviations: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet and br=broad, are used in reporting the spectra. Infrared spectra were obtained using a JASCO FTIR-460 PLUS spectrometer. Column chromatography was performed using Silica gel Kiesegel 60 with particle size 40–63 μm (230–400 mesh) by preparing the slurry with the eluent mixture and packing into a chromatography column. The collected samples

were analysed by TLC. Compounds are numbered according to Schemes 1 and 2.

Identification of the liquid crystalline phases was based on the type of texture exhibited by the compound. The textures were observed with a polarizing optical microscope Zeiss Axio Imager A2m equipped with a Linkam hot stage.

The identification was confirmed by X-ray studies carried out on a Bruker GADDS system equipped with Vantec 2000 area detector and hot stage controlled by Linkam controller, and on a Bruker D8 Discover system equipped with Anton Paar DCS-350 heating stage. In both systems Cu Kα radiation was used.

Phase transition temperatures, enthalpies and melting points were determined by differential scanning calorimetry measurements performed on TA Instruments DSC Q 200. Only for compound **10c**, the temperature of the nematic to smectic A phase transition was determined on the basis of polarizing optical microscopy and X-ray measurements. This phase transition was not detectable by the DSC measurement.

Absorption spectra were recorded on a Shimadzu UV-3101PC spectrometer. Emission spectra were measured with FluoroLog FL3-2-IHR320 HORIBA Jobin Yvon spectrofluorometer equipped with a TBX-04 PMT detector. Both chloroform solutions ($c=3.2\times10^{-5}$ mol dm^{-3}) and solid state samples were excited at 360 nm. For fluorescence quantum yield measurements an ethanol solution of anthracene was used as a standard.[30] Fluorescence decay was measured by time-correlated single-photon counting system using the same FluoroLog fluorometer and Horiba-Jobin Yvon NanoLED 340 pulse diode light source with peak wavelength at 335 nm.

Electrochemical data were obtained with cyclic voltammetry and differential pulse voltammetry techniques using a three-electrode cell and an electrochemical workstation CH instruments 750 B. The working electrode was a glass carbon electrode, the auxiliary electrode was a Pt wire, and Ag/Ag$^+$ was used as a reference electrode. Tetrabutylammonium hexafluorophosphate (TBAHFP) 0.1 M was used as supporting electrolyte in CH_2Cl_2. Ferrocenium/ferrocene (Fc/Fc$^+$) redox couple was used as a potential reference. The potentials versus Normal Hydrogen Electrode (NHE) were calculated by addition of 700 mV to the potentials versus Fc/Fc$^+$.[31]

4.2. Typical procedure for the alkylation of 1

4′-Hydroxybiphenyl-4-carbonitrile (**1**) (20.0 g, 0.1 mol), potassium carbonate (28.0 g, 0.2 mol) and DMF (600 mL) were placed in a 1000 mL flask and stirred. The corresponding alkylbromide (20.0 g for 1-bromohexane, 23.0 g for 1-bromo-octane, 0.12 mol) was added and the reaction mixture was heated at 120 °C for 48 h. The mixture was then cooled to room temperature and poured onto ice water (1000 mL) and left to stand overnight. The precipitated product was isolated by filtration and crystallized from ethanol.

4.2.1. 4′-Hexyloxybiphenyl-4-carbonitrile ***2a***. Yield: 85% (24.0 g), white crystals. Analytical data corresponds to those published for 4′-hexyloxybiphenyl-4-carbonitrile, $C_{19}H_{21}NO$ (279.38).[32]

4.2.2. 4′-Octyloxybiphenyl-4-carbonitrile ***2b***. Yield: 88% (27.0 g), white crystals. Analytical data corresponds to those published for 4′-octyloxybiphenyl-4-carbonitrile, $C_{21}H_{25}NO$ (307.43).[32]

4.3. The Grignard reaction of 2a and 2b

To an evacuated 1000 mL three necked round bottomed flask magnesium (1.2 g, 0.05 mol) and dry diethylether (15 mL) were placed. To the stirred mixture a 2.0 M solution of methyl iodide (7.1 g, 3.0 mL, 0.05 mol) in diethylether was added dropwise over 40 min. The resulting solution of methylmagnesium iodide was stirred at room temperature for 1 h. The solution of starting 4′-alkyloxy-4-carbonitrile **2a** or **2b** (9.1 g for **2a**, 10.0 g for **2b**, 0.0325 mol) in diethylether (400 mL) was added to a mixture of methylmagnesium iodide and heated at the boiling temperature of diethylether for 6 h, then the flask was cooled and distilled water (300 mL) was added slowly. The mixture was left to stir for an additional 30 min. The aqueous and etheric layers were separated, water phase was extracted with diethylether (2×250 mL). The combined organic phase was dried with $MgSO_4$ and evaporated. The crude product was purified by column chromatography on silica gel eluting with dichloromethane.

4.3.1. 1-(4′-Hexyloxy-biphenyl-4-yl)-ethanone ***3a***. Yield: 52% (5.0 g), white crystals; mp=135–140 °C; R_f (CH_2Cl_2) 0.68; δ_H (500 MHz $CDCl_3$): 7.99 (d, J=8.6 Hz, 2H), 7.64–7.52 (m, 4H), 6.87 (d, J=8.6 Hz, 2H), 3.97 (t, J=6.2 Hz, 2H, CH_2), 2.61 (s, 3H, $COCH_3$), 1.76 (q, J=6.2 Hz, 2H, CH_2), 1.24 (br s, 6H, 3× CH_2), 0.89 (t, J=6.2 Hz, 3H, CH_3); δ_C (125 MHz $CDCl_3$): 197.6, 159.6, 145.4, 135.5, 132.0, 128.7, 128.1, 127.7, 115.1, 69.9, 31.4, 30.1, 26.3, 24.1, 22.7, 13.9; ν_{max}(KBr) 3124, 2928, 1705 (C=O), 1615, 1455, 782, 647 cm^{-1}; Anal. Calcd for $C_{20}H_{24}O_2$ (296.4): C, 81.04; H, 8.16%. Found: C, 81.12; H, 8.22%. Mass (ESI) m/z (%) 296.2.

4.3.2. 1-(4′-Octyloxy-biphenyl-4-yl)-ethanone ***3b***. Yield: 50% (5.3 g), white crystals; mp=115–118 °C; R_f (CH_2Cl_2) 0.70; δ_H (500 MHz $CDCl_3$): 7.95 (d, J=8.4 Hz, 2H), 7.62–7.56 (m, 4H), 6.84 (d, J=8.4 Hz, 2H), 3.89 (t, J=6.4 Hz, 2H, CH_2), 2.58 (s, 3H, $COCH_3$), 1.72 (q, J=6.4 Hz, 2H, CH_2), 1.30 (q, J=6.4 Hz, 2H, CH_2), 1.27 (br s, 8H, 4× CH_2), 0.84 (t, J=6.4 Hz, 3H, CH_3); δ_C (125 MHz $CDCl_3$): 196.9, 158.4, 146.0, 135.7, 131.9, 129.0, 128.6, 128.2, 127.4, 114.7, 70.2, 31.5, 30.4, 29.9, 26.6, 23.8, 22.4, 14.0; ν_{max}(KBr) 3099, 2943, 1715 (C=O), 1607, 1454, 764, 632 cm^{-1}; Anal. Calcd for $C_{22}H_{28}O_2$ (324.46): C, 81.44; H, 8.70%. Found: C, 81.70; H, 8.92%. Mass (ESI) m/z (%) 324.60.

4.4. Knoevenagel condensation of 3a and 3b

1-(4′-Alkyloxy-biphenyl-4-yl)-ethanone **3a** or **3b** (3.0 g for **3a**, 3.2 g for **3b**, 10.0 mmol) and methylcyanoacetate (2.0 g, 1.8 mL, 20.0 mmol) were dissolved in dry toluene (100 mL). Trimethylsilylacetate (2.0 g, 2.2 mL, 15.0 mmol) and NH_4OAc (0.8 g, 10.0 mmol) were added and the mixture was heated at 80 °C for 12 h. After the reaction was complete, the mixture was cooled to room temperature and diluted with water (80 mL). The aqueous layer was separated and extracted with toluene (2×50 mL). The combined organic extracts were dried with $MgSO_4$ and evaporated. Products **4a** and **4b** were isolated and purified by column chromatography on silica gel eluting with dichloromethane and isolated as a mixture of *E*/*Z* isomers.

4.4.1. (E/Z) 2-Cyano-3-(4′-hexyloxy-biphenyl-4-yl)-but-2-enoic acid methyl ester ***4a***. Yield: 58% (2.2 g), yellow solid; mp=82–86 °C; R_f (CH_2Cl_2) 0.82; δ_H (500 MHz $CDCl_3$): 8.01 (d, J=8.2 Hz, 2H), 7.66–7.50 (m, 4H), 6.84 (d, J=8.2 Hz, 2H), 4.02 (t, J=6.6 Hz, 2H, CH_2), 3.96 (s, 3H, $COOCH_3$), 1.83 (s, 3H, CH_3), 1.77 (q, J=6.6 Hz, 2H, CH_2), 1.27 (br s, 6H, 3× CH_2), 0.88 (t, J=6.6 Hz, 3H, CH_3); δ_C (125 MHz $CDCl_3$): 172.0, 161.9, 157.6, 135.1, 132.8, 127.9, 127.2, 126.1, 125.3, 117.6, 113.9, 101.9, 67.1, 51.7, 31.3, 30.9, 28.6, 25.0, 18.2, 13.1; ν_{max}(KBr) 3116, 2956, 2247 (C≡N), 1694 (C=O$_{ester}$), 1628 (C=C), 1216 (C–O$_{ester}$), 1467, 782, 588 cm^{-1}; Anal. Calcd for $C_{24}H_{27}NO_3$ (377.48): C, 76.36; H, 7.21; N, 3.71%. Found: C, 76.48; H, 7.15; N, 3.84%. Mass (ESI) m/z (%) 378.40 [M+H]$^+$.

4.4.2. (E/Z) 2-Cyano-3-(4′-octyloxy-biphenyl-4-yl)-but-2-enoic acid methyl ester ***4b***. Yield: 61% (2.5 g), yellow solid; mp=74–77 °C; R_f (CH_2Cl_2) 0.80; δ_H (500 MHz $CDCl_3$): 8.12 (d, J=8.6 Hz, 2H), 7.72–7.54 (m, 4H), 6.87 (d, J=8.6 Hz, 2H), 3.98 (t, J=6.6 Hz, 2H, CH_2), 3.88 (s, 3H, $COOCH_3$), 1.87 (s, 3H, CH_3), 1.74 (q, J=6.6 Hz, 2H, CH_2), 1.38 (q, J=6.6 Hz, 2H, CH_2), 1.30 (br s, 8H, 3× CH_2), 0.86 (t, J=6.6 Hz, 3H, CH_3); δ_C (125 MHz $CDCl_3$): 169.7, 162.2, 156.9, 135.3, 133.0, 128.1,

127.9, 127.1, 124.8, 117.4, 114.0, 102.0, 68.2, 52.1, 32.0, 31.1, 30.6, 29.9, 28.7, 24.6, 17.8, 13.9; ν_{max}(KBr) 3129, 2944, 2239 (C≡N), 1698 (C=O_{ester}), 1642 (C=C), 1214 (C–O_{ester}), 1457, 776, 596 cm^{-1}; Anal. Calcd for $C_{26}H_{31}NO_3$ (405.53): C, 77.01; H, 7.71; N, 3.45%. Found: C, 77.23; H, 7.66; N, 3.52%. Mass (ESI) *m*/*z* (%) 406.24 $[M+H]^+$, 428.30 $[M+Na]^+$.

4.5. Gewald reaction: synthesis of β-alkyloxybiphenyl substituted 2-aminothiophenes 5a, 5b

General procedure A. To a solution of (*E*/*Z*) 2-cyano-3-(4′-hexyloxy-biphenyl-4-yl)-but-2-enoic acid methyl ester **4a** (2.0 g, 5.5 mmol) or (*E*/*Z*) 2-cyano-3-(4′-octyloxy-biphenyl-4-yl)-but-2-enoic acid methyl ester **4b** (2.2 g, 5.5 mmol) in methanol (30 mL), sulfur (350 mg, 11.0 mmol) and triethylamine (1.22 g, 1.70 mL, 12.1 mmol) were added. After stirring at 45 °C for 12 h, the reaction mixture was evaporated and the crude product was purified by column chromatography on silica gel (absorbed with 1% triethylamine) eluting with a mixture of hexanes/ethylacetate (80:20).

General procedure B. To a solution of (*E*/*Z*) 2-cyano-3-(4′-hexyloxy-biphenyl-4-yl)-but-2-enoic acid methyl ester **4a** (2.0 g, 5.5 mmol) or (*E*/*Z*) 2-cyano-3-(4′-octyloxy-biphenyl-4-yl)-but-2-enoic acid methyl ester **4b** (2.2 g, 5.5 mmol) in methanol (30 mL), sulfur (350 mg, 11.0 mmol) and morpholine (1.10 g, 1.10 mL, 12.1 mmol) were added. After stirring at 45 °C for 8–12 h, the reaction mixture was evaporated and the crude product was purified by column chromatography on silica gel (absorbed with 1% triethylamine) eluting with a mixture of hexanes/ethylacetate (80:20).

General procedure C. To a solution of (*E*/*Z*) 2-cyano-3-(4′-hexyloxy-biphenyl-4-yl)-but-2-enoic acid methyl ester **4a** (2.0 g, 5.5 mmol) or (*E*/*Z*) 2-cyano-3-(4′-octyloxy-biphenyl-4-yl)-but-2-enoic acid methyl ester **4b** (2.2 g, 5.5 mmol) in tetrahydrofuran (30 mL), sulfur (350 mg, 11.0 mmol) and morpholine (1.20 g, 1.20 mL, 14.0 mmol) were added. After stirring at 50 °C for 12 h, the reaction mixture was evaporated and the crude product was purified by column chromatography on silica gel (absorbed with 1% triethylamine) eluting with a mixture of hexanes/ethylacetate (80:20).

4.5.1. 2-Amino-4-(4′-hexyloxy-biphenyl-4-yl)-thiophene-3-carboxylic acid methyl ester ***5a***. Yield: 28% (630 mg)—*Method A*; 40% (900 mg)—*Method B*; 60% (1.4 g)—*Method C*; white solid, mp=120–124 °C; R_f (hexanes/EtOAc/80:20) 0.46; δ_H (500 MHz $CDCl_3$): 7.56–7.49 (m, 4H), 7.35 (d, *J*=8.4 Hz, 2H), 6.97 (d, *J*=8.4 Hz, 2H), 6.12 (s, 1H, $H_{thiophene}$), 6.08 (br s, 2H, NH_2), 4.00 (t, *J*=6.5 Hz, 2H, CH_2), 3.60 (s, 3H, $COOCH_3$), 1.81 (q, *J*=6.5 Hz, 2H, CH_2), 1.48–1.44 (m, 2H, CH_2), 1.27 (br s, 4H, 2× CH_2), 0.884 (t, *J*=6.5 Hz, 3H, CH_3); δ_C (125 MHz $CDCl_3$): 163.5, 156.7, 140.3, 136.6, 134.8, 130.0, 128.6, 128.0, 127.5, 127.1, 122.0, 115.2, 105.8, 74.3, 49.5, 33.1, 30.9, 26.4, 24.4, 12.8; ν_{max}(KBr) 3343 (NH_2), 3115, 2952, 1691 (C=O_{ester}), 1222 (C–O_{ester}), 1478, 840, 603 cm^{-1}; Anal. Calcd for $C_{24}H_{27}NO_3S$ (409.54): C, 70.39; H, 6.65; N, 3.42; S, 7.83%. Found: C, 70.77; H, 6.50; N, 3.72; S, 7.66%. Mass (ESI) *m*/*z* (%) 409.3.

4.5.2. 2-Amino-4-(4′-octyloxy-biphenyl-4-yl)-thiophene-3-carboxylic acid methyl ester ***5b***. Yield: 30% (722 mg)—*Method A*; 39% (940 mg)—*Method B*; 64% (1.5 g)—*Method C*; white solid, mp=105–108 °C; R_f (hexanes/EtOAc/80:20) 0.48; δ_H (500 MHz $CDCl_3$): 7.99 (d, *J*=8.4 Hz, 2H), 7.67–7.59 (m, 4H), 6.97 (d, *J*=8.4 Hz, 2H), 6.10 (s, 1H, $H_{thiophene}$), 6.04 (br s, 2H, NH_2), 4.00 (t, *J*=6.6 Hz, 2H, CH_2), 3.60 (s, 3H, $COOCH_3$), 1.81 (q, *J*=6.6 Hz, 2H, CH_2), 1.32 (q, *J*=6.6 Hz, 2H, CH_2), 1.29 (br s, 8H, 4× CH_2), 0.89 (t, *J*=6.6 Hz, 3H, CH_3); δ_C (125 MHz $CDCl_3$): 162.2, 155.9, 141.0, 137.1, 135.0, 129.7, 129.1, 128.0, 127.6, 125.6, 121.6, 114.8, 105.9, 72.3, 50.1, 31.8, 27.1, 29.6, 29.3, 26.6, 24.2, 14.1; ν_{max}(KBr) 3321 (NH_2), 3067, 2943, 1696 (C=O_{ester}), 1209 (C–O_{ester}), 1465, 872, 577 cm^{-1}; Anal. Calcd for $C_{26}H_{31}NO_3S$ (437.59): C, 71.36; H, 7.14; N, 3.20; S, 7.33%. Found: C, 71.40; H, 7.15; N, 3.25; S, 7.36%. Mass (ESI) *m*/*z* (%) 438.2 $[M+H]^+$.

4.6. Typical procedure for the synthesis of 4-alkyloxybenzaldehydes 7a–d

4-Hydroxybenzaldehyde (12.5 g, 0.1 mol), potassium carbonate (16.5 g, 0.12 mol) and dimethylformamide (300 mL) were placed in a three-necked 1 L round bottomed flask. The reaction mixture was heated to 80 °C and stirred. To the warm solution the appropriate alkylbromide (19.8 g for 1-bromohexane; 23.2 g for 1-bromooctane; 26.5 g for 1-bromodecane; 29.9 g for 1-bromododecane; 0.12 mol) was added dropwise over 1 h. The mixture was then heated at 80 °C for 8 h. After cooling down to room temperature the mixture was diluted with water (300 mL). The aqueous phase was extracted with dichloromethane (3×300 mL). The combined organic layer was washed twice with aq NaOH (10%mol), water and dried with $MgSO_4$. After evaporation of solvent on a rotary evaporator the corresponding products were obtained as pale yellow oils, which were subsequently used without purification.

4.6.1. 4-Hexyloxybenzaldehyde ***7a***. Yield: 94% (19.4 g), yellow oil. Analytical data corresponds to those published for 4-hexyloxybenzaldehyde, $C_{13}H_{18}O_2$ (206.28).[33]

4.6.2. 4-Octyloxybenzaldehyde ***7b***. Yield: 91% (21.3 g), yellow oil. Analytical data corresponds to those published for 4-octyloxybenzaldehyde, $C_{15}H_{22}O_2$ (234.33).[19]

4.6.3. 4-Decyloxybenzaldehyde ***7c***. Yield: 89% (23.4 g), yellow oil. Analytical data corresponds to those published for 4-decyloxybenzaldehyde, $C_{17}H_{26}O_2$ (262.39).[33]

4.6.4. 4-Dodecyloxybenzaldehyde ***7d***. Yield: 90% (26.1 g), yellow oil; δ_H (500 MHz $CDCl_3$): 9.65 (s, 1H, CHO), 7.78 (d, *J*=8.3 Hz, 2H), 7.34 (d, *J*=8.3 Hz, 2H), 4.12 (t, *J*=6.6 Hz, 2H, CH_2), 1.88–1.74 (m, 2H, CH_2), 1.48–1.42 (m, 2H, CH_2), 1.26 (br s, 16H, 8× CH_2), 0.88 (t, *J*=6.6 Hz, 3H, CH_3); δ_C (125 MHz $CDCl_3$): 189.8, 159.7, 130.6, 130.1, 128.4, 112.6, 69.7, 32.1, 30.2, 29.7, 29.4, 29.0, 28.6, 28.4, 26.1, 22.8, 14.2; ν_{max}(KBr) 2956, 2920, 2812, 1698 (C=O), 1600, 1468, 675 cm^{-1}; Anal. Calcd for $C_{19}H_{30}O_2$ (290.44): C, 78.57, H, 10.41%. Found: C, 78.31, H, 10.70%. Mass (ESI) *m*/*z* (%) 290.8.

4.7. Wittig reaction: synthesis of substituted stilbenes 8a–d[20]

To a solution of methyl (4-triphenylphosphoniummethyl)-benzoate bromide[34] (6.0 g, 12.0 mmol), dissolved in dry dichloromethane (70 mL) and tetrahydrofuran (70 mL), anhydrous potassium carbonate (8.4 g, 61.0 mmol) followed by 18-crown-6 (20 mg, 0.07 mmol) were added. The reaction mixture was stirred at room temperature for 1 h. The appropriate 4-alkyloxybenzaldehyde **7a**–**d** (3.7 g for **7a**, 4.2 g for **7b**, 4.7 g for **7c**, 5.2 g for **7d**, 18.0 mmol) was added and the reaction mixture was heated at the boiling temperature of dichloromethane–THF solvent mixture for 20 h. After filtration of inorganic salts formed during reaction, the mixture was evaporated and the crude product was crystallized from ethanol. According to spectral data, only (*E*)-stilbene was crystallized from the reaction mixture in all cases.

4.7.1. (E) 4-[2-(4-Hexyloxy-phenyl)-vinyl]-benzoic acid methyl ester ***8a***. Yield: 63% (3.8 g), pale yellowish solid; mp=144–146 °C; δ_H (500 MHz $CDCl_3$): 8.03 (d, *J*=8.1 Hz, 2H), 7.66 (d, *J*=8.3 Hz, 2H), 7.59 (d, *J*=8.1 Hz, 2H), 7.55 (d, *J*=16.2 Hz, 1H), 7.51 (d, *J*=16.2 Hz, 1H), 6.95 (d, *J*=8.3 Hz, 2H), 4.06 (t, *J*=6.6 Hz, 2H, CH_2), 3.95 (s, 3H, $COOCH_3$), 1.57 (t, *J*=6.6 Hz, 2H, CH_2), 1.26 (br s, 6H, 3× CH_2), 0.882

(t, J=6.6 Hz, 3H, CH_3); δ_C (125 MHz $CDCl_3$): 167.1, 156.7, 140.2, 129.7, 128.8, 127.9, 126.7, 126.4, 124.1, 123.8, 113.5, 71.0, 52.2, 32.1, 30.0, 26.1, 22.9, 14.2; ν_{max}(KBr) 2925, 2864, 1715 (C=O_{ester}), 1596 (C=C), 1475, 1286 (C–O_{ester}), 1468, 822, 654 cm^{-1}; Anal. Calcd for $C_{22}H_{26}O_3$ (338.44): C, 78.07; H, 7.74%. Found: C, 78.2; H, 7.83%. Mass (ESI) m/z (%) 338.2.

4.7.2. (E) 4-[2-(4-Octyloxy-phenyl)-vinyl]-benzoic acid methyl ester ***8b***. Yield: 59% (3.9 g), pale yellowish solid; mp=132–130 °C; δ_H (500 MHz $CDCl_3$): 8.00 (d, J=8.1 Hz, 2H), 7.66 (d, J=8.1 Hz, 2H), 7.56 (d, J=8.1 Hz, 2H), 7.48 (d, J=16.2 Hz, 1H), 7.35 (d, J=16.2 Hz, 1H), 6.91 (d, J=8.1 Hz, 2H), 3.98 (t, J=6.2 Hz, 2H, CH_2), 3.92 (s, 3H, $COOCH_3$), 1.66 (t, J=6.2 Hz, 2H, CH_2), 1.35 (q, J=6.2 Hz, 2H, CH_2), 1.29 (br s, 8H, 4× CH_2), 0.91 (t, J=6.2 Hz, 3H, CH_3); δ_C (125 MHz $CDCl_3$): 166.9, 157.9, 139.8, 129.6, 128.7, 128.0, 127.5, 126.4, 125.8, 123.9, 123.1, 114.0, 73.1, 51.9, 31.5, 30.8, 29.9, 26.1, 23.0, 13.8; ν_{max}(KBr) 2936, 2879, 1723 (C=O_{ester}), 1602 (C=C), 1451, 1269 (C–O_{ester}), 1454, 856, 692 cm^{-1}; Anal. Calcd for $C_{24}H_{30}O_3$ (366.49): C, 78.65; H, 8.25%. Found: C, 79.0; H, 8.32%. Mass (ESI) m/z (%) 366.2.

4.7.3. (E) 4-[2-(4-Decyloxy-phenyl)-vinyl]-benzoic acid methyl ester ***8c***. Yield: 54% (3.8 g), yellowish solid; mp=124–126 °C; δ_H (500 MHz $CDCl_3$): 8.06 (d, J=8.4 Hz, 2H), 7.70 (d, J=8.3 Hz, 2H), 7.54 (d, J=8.3 Hz, 2H), 7.60 (d, J=16.4 Hz, 1H), 7.41 (d, J=16.4 Hz, 1H), 7.00 (d, J=8.4 Hz, 2H), 4.00 (q, J=6.4 Hz, 2H, CH_2), 3.96 (s, 3H, $COOCH_3$), 1.72 (t, J=6.4 Hz, 2H, CH_2), 1.41–1.37 (m, 2H, CH_2), 1.27 (br s, 12H, 6× CH_2), 0.87 (t, J=6.4 Hz, 3H, CH_3); δ_C (125 MHz $CDCl_3$): 167.3, 158.2, 141.0, 130.6, 129.1, 128.5, 127.3, 126.7, 126.0, 124.0, 123.3, 113.7, 71.2, 50.5, 32.0, 30.1, 29.9, 29.5, 26.9, 26.0, 22.8, 15.1; ν_{max}(KBr) 2944, 2860, 1718 (C=O_{ester}), 1612 (C=C), 1468, 1264 (C–O_{ester}), 1476, 822, 665 cm^{-1}; Anal. Calcd for $C_{26}H_{34}O_3$ (394.55): C, 79.15; H, 8.69%. Found: C, 79.3; H, 8.30%. Mass (ESI) m/z (%) 394.1.

4.7.4. (E) 4-[2-(4-Dodecyloxy-phenyl)-vinyl]-benzoic acid methyl ester ***8d***. Yield: 45% (3.4 g), pale grey solid; mp=112–115 °C; δ_H (500 MHz $CDCl_3$): 7.97 (d, J=8.2 Hz, 2H), 7.70 (d, J=8.2 Hz, 2H), 7.61 (d, J=8.1 Hz, 2H), 7.36 (d, J=16.5 Hz, 1H), 7.21 (d, J=16.5 Hz, 1H), 6.85 (d, J=8.1 Hz, 2H), 3.99 (s, 3H, $COOCH_3$), 3.96 (t, J=6.6 Hz, 2H, CH_2), 1.74–1.70 (m, 2H, CH_2), 1.31 (q, J=6.6 Hz, 2H, CH_2), 1.26 (br s, 16H, 8× CH_2), 0.86 (t, J=6.6 Hz, 3H, CH_3); δ_C (125 MHz $CDCl_3$): 166.9, 157.9, 139.8, 129.6, 128.7, 128.0, 127.5, 126.4, 125.8, 123.9, 123.1, 114.0, 73.1, 51.9, 31.6, 30.8, 30.4, 29.9, 29.6, 29.4, 28.2, 26.1, 23.0, 13.8; ν_{max}(KBr) 2952, 2842, 1702 (C=O_{ester}), 1625 (C=C), 1480, 1245 (C–O_{ester}), 1482, 890, 676 cm^{-1}; Anal. Calcd for $C_{28}H_{38}O_3$ (422.60): C, 79.58; H, 9.06%. Found: C, 79.9; H, 9.25%. Mass (ESI) m/z (%) 422.3.

4.8. Standard procedure for the synthesis of acyl chlorides 9a–d[21]

To a solution of the appropriate (*E*) 4-[2-(4-alkyloxy-phenyl)-vinyl]-benzoic acid methyl ester **8a–d** (2.4 g for **8a**, 2.6 g for **8b**, 2.8 g for **8c**, 3.0 g for **8d**, 7.0 mmol) in ethanol (200 mL), a solution of potassium hydroxide (1.6 g, 28.0 mmol) in water (20 mL) was added and the mixture was heated at the boiling temperature of ethanol for 12 h. After cooling the solution, the crude product was isolated by suction filtration as the potassium salt. After drying under vacuum, the obtained salt was suspended in toluene (200 mL) and treated with an excess of oxalyl chloride (6.0 mL). The reaction mixture was heated at 110 °C for 8 h. After filtration of the precipitated potassium chloride, the remaining solution was evaporated to dryness. The products slowly solidified at room temperature and were subsequently used without further purification and characterization in the next step.

4.8.1. 4-[2-(4-Hexyloxy-phenyl)-vinyl]-benzoyl chloride ***9a***. Yield 96% (2.3 g), bright yellow solid, $C_{21}H_{23}ClO_2$ (342.86).

4.8.2. 4-[2-(4-Octyloxy-phenyl)-vinyl]-benzoyl chloride ***9b***. Yield 98% (2.5 g), bright yellow solid, $C_{23}H_{27}ClO_2$ (370.91).

4.8.3. 4-[2-(4-Decyloxy-phenyl)-vinyl]-benzoyl chloride ***9c***. Yield 94% (2.6 g), bright yellow solid, $C_{25}H_{31}ClO_2$ (398.97).

4.8.4. 4-[2-(4-Dodecyloxy-phenyl)-vinyl]-benzoyl chloride ***9d***. Yield 90% (2.7 g), bright yellow solid, $C_{27}H_{35}ClO_2$ (427.02).

4.9. Synthesis of final 2-aminothiophene-stilbene containing mesogens 10a–f

To a solution of 2-amino-4-(4′-alkyloxy-biphenyl-4-yl)-thiophene-3-carboxylic acid methyl ester **5a** or **5b** (614 mg for **5a**, 660 mg for **5b**,1.5 mmol), DMAP (20 mg, 0.16 mmol), triethylamine (few drops) in toluene (50 mL) the appropriate 4-[2-(4-alkyloxy-phenyl)-vinyl]-benzoyl chloride **9a–d** (1030 mg for **9a**, 1110 mg for **9b**, 1200 mg for **9c**, 1300 mg for **9d**, 3.0 mmol) was added. The reaction mixture was stirred at the boiling temperature of toluene for 12–24 h, then the excess of solvent was evaporated and the remaining oil was purified by column chromatography on silica gel (absorbed with 1% triethylamine) eluting with dichloromethane. The range of product yields in this step varied from 35 to 45 %.

4.9.1. 4-(4′-Hexyloxy-biphenyl-4-yl)-2-{4-[2-(4-hexyloxy-phenyl)-vinyl]-benzoylamino}-thiophene-3-carboxylic acid methyl ester ***10a***. Yield: 42% (451 mg), yellow solid; mp=169–172 °C; R_f (CH_2Cl_2) 0.80; δ_H (500 MHz $CDCl_3$): 12.36 (br s, 1H, NH), 8.03 (d, J=8.6 Hz, 2H), 7.63 (d, J=8.6 Hz, 2H), 7.59 (d, J=8.0 Hz, 2H), 7.57 (d, J=8.0 Hz, 2H), 7.49 (d, J=8.0 Hz, 2H), 7.38 (d, J=8.0 Hz, 2H), 7.21 (d, J=16.2 Hz, 1H), 7.01 (d, J=16.2 Hz, 1H), 6.99 (d, J=8.0 Hz, 2H), 6.91 (d, J=8.0 Hz, 2H), 6.70 (s, 1H, $H_{thiophene}$), 4.00 (t, J=6.6 Hz, 4H, 2× CH_2), 3.69 (s, 3H, $COOCH_3$), 1.85 (q, J=6.6 Hz, 4H, 2× CH_2), 1.50 (q, J=6.6 Hz, 4H, 2× CH_2), 1.37 (br s, 8H, 4× CH_2), 0.92 (t, J=6.6 Hz, 6H, 3× CH_3); δ_C (125 MHz $CDCl_3$): 167.1, 163.5, 158.8, 153.2, 151.0, 145.2, 139.4, 135.9, 133.0, 132.2, 130.0, 128.6, 128.2, 127.9, 127.5, 127.1, 126.5, 126.1, 125.7, 124.3, 122.7, 114.8, 113.0, 111.4, 110.6, 71.1, 69.1, 51.4, 32.2, 31.9, 29.7, 26.0, 25.4, 23.0, 22.7, 14.1, 13.8; ν_{max}(KBr) 3485 (NH), 3184, 3079, 2950, 2933, 2864, 1705 (C=O_{ester}), 1665 (C=O_{amide}), 1638 (C=C), 1456, 1317, 1270 (C–O_{ester}), 905, 780, 694, 633 cm^{-1}; Anal. Calcd for $C_{45}H_{49}NO_5S$ (715.94): C, 75.49, H, 6.90, N, 1.96, S, 4.48%. Found: C, 75.60, H, 6.72, N, 2.05, S, 4.50%. Mass (ESI) m/z (%) 716.4 $[M+H]^+$.

4.9.2. 4-(4′-Hexyloxy-biphenyl-4-yl)-2-{4-[2-(4-octyloxy-phenyl)-vinyl]-benzoylamino}-thiophene-3-carboxylic acid methyl ester ***10b***. Yield: 45% (502 mg), yellow solid; mp=162–165 °C; R_f (CH_2Cl_2) 0.76; δ_H (500 MHz $CDCl_3$): 12.29 (br s, 1H, NH), 7.92 (d, J=8.4 Hz, 2H), 7.60–7.54 (m, 4H), 7.36 (d, J=8.4 Hz, 2H), 7.32 (d, J=8.2 Hz, 2H), 7.27 (d, J=8.2 Hz, 2H), 7.21 (d, J=16.0 Hz, 1H), 7.08 (d, J=16.0 Hz, 1H), 6.97 (d, J=8.0 Hz, 2H), 6.91 (d, J=8.0 Hz, 2H), 6.67 (s, 1H, $H_{thiophene}$), 4.02 (t, J=6.4 Hz, 2H, CH_2), 3.99 (t, J=6.4 Hz, 2H, CH_2), 3.69 (s, 3H, $COOCH_3$), 1.85 (q, J=6.2 Hz, 4H, 2× CH_2), 1.33 (q, J=6.4 Hz, 2H, CH_2), 1.27 (br s, 6H, 3× CH_2), 1.24 (br s, 8H, 4× CH_2), 0.92 (t, J=6.2 Hz, 3H, CH_3), 0.89 (t, J=6.2 Hz, 3H, CH_3); δ_C (125 MHz $CDCl_3$): 166.8, 162.9, 158.2, 153.4, 150.3, 146.1, 139.0, 135.5, 132.8, 131.9, 130.2, 129.0, 128.4, 128.1, 127.8, 126.9, 126.4, 127.5, 127.1, 126.1, 124.6, 123.2, 114.6, 112.9, 111.7, 110.3, 72.3, 70.2, 52.2, 32.1, 30.9, 30.3, 29.7, 26.6, 26.0, 23.3, 22.8, 14.4, 13.7; ν_{max}(KBr) 3476 (NH), 3205, 3099, 2966, 2948, 2886, 1724 (C=O_{ester}), 1678 (C=O_{amide}), 1644 (C=C), 1460, 1326, 1274 (C–O_{ester}), 894, 755, 672, 650 cm^{-1}; Anal. Calcd for $C_{47}H_{53}NO_5S$ (743.99): C, 75.87, H, 7.18, N,

1.88, S, 4.31%. Found: C, 76.01, H, 7.31, N, 1.75, S, 4.60%. Mass (ESI) *m*/*z* (%) 743.50.

4.9.3. 2-{4-[2-(4-Hexyloxy-phenyl)-vinyl]-benzoylamino}-4-(4′-octyloxy-biphenyl-4-yl)-thiophene-3-carboxylic acid methyl ester ***10c***. Yield: 40% (446 mg), yellow solid; mp=165–167 °C; R_f (CH_2Cl_2) 0.74; δ_H (500 MHz $CDCl_3$): 12.35 (br s, 1H, NH), 8.03 (d, *J*=8.3 Hz, 2H), 7.64 (d, *J*=8.3 Hz, 2H), 7.59–7.55 (m, 4H), 7.48 (d, *J*=8.1 Hz, 2H), 7.38 (d, *J*=8.1 Hz, 2H), 7.20 (d, *J*=16.5 Hz, 1H), 7.02 (d, *J*=16.5 Hz, 1H), 6.98 (d, *J*=8.1 Hz, 2H), 6.92 (d, *J*=8.1 Hz, 2H), 6.69 (s, 1H, $H_{thiophene}$), 4.01 (t, *J*=6.4 Hz, 2H, CH_2), 3.99 (t, *J*=6.4 Hz, 2H, CH_2), 3.69 (s, 3H, $COOCH_3$), 1.81 (q, *J*=6.6 Hz, 4H, 2× CH_2), 1.48 (q, *J*=6.6 Hz, 2H, CH_2), 1.27 (br s, 6H, 3× CH_2), 1.25 (br s, 8H, 4× CH_2), 0.93 (t, *J*=6.4 Hz, 3H, CH_3), 0.89 (t, *J*=6.4 Hz, 3H, CH_3); δ_C (125 MHz $CDCl_3$): 167.0, 163.1, 158.6, 153.1, 146.1, 139.4, 135.7, 133.0, 132.3, 130.1, 129.4, 128.4, 128.1, 127.6, 127.1, 126.5, 126.1, 125.7, 124.9, 122.6, 114.7, 113.9, 111.6, 110.2, 71.4, 70.7, 51.6, 32.1, 31.0, 30.5, 30.1, 29.6, 29.4, 26.2, 25.9, 23.4, 22.5, 14.4, 13.9; ν_{max}(KBr) 3472 (NH), 3202, 3094, 2944, 2929, 2881, 1712 (C=O_{ester}), 1681 (C=O_{amide}), 1624 (C=C), 1468, 1324, 1257 (C–O_{ester}), 898, 776, 657, 609 cm^{-1}; Anal. Calcd for $C_{47}H_{53}NO_5S$ (743.99): C, 75.87, H, 7.18, N, 1.88, S, 4.31%. Found: C, 75.55, H, 7.24, N, 1.94, S, 4.20%. Mass (ESI) *m*/*z* (%) 745.00 $[M+H]^+$.

4.9.4. 4-(4′-Octyloxy-biphenyl-4-yl)-2-{4-[2-(4-octyloxy-phenyl)-vinyl]-benzoylamino}-thiophene-3-carboxylic acid methyl ester ***10d***. Yield: 42% (486 mg), yellow solid; mp=168–172 °C; R_f (CH_2Cl_2) 0.69; δ_H (500 MHz $CDCl_3$): 12.36 (br s, 1H, NH), 8.03 (d, *J*=8.3 Hz, 2H), 7.63 (d, *J*=8.6 Hz, 2H), 7.60 (d, *J*=8.2 Hz, 2H), 7.56 (d, *J*=8.2 Hz, 2H), 7.49 (d, *J*=8.3 Hz, 2H), 7.38 (d, *J*=8.4 Hz, 2H), 7.20 (d, *J*=16.4 Hz, 1H), 7.03 (d, *J*=8.0 Hz, 2H), 7.02 (d, *J*=16.4 Hz, 1H), 6.91 (d, *J*=8.4 Hz, 2H), 6.70 (s, 1H, $H_{thiophene}$), 4.00 (t, *J*=6.6 Hz, 4H, 2× CH_2), 3.69 (s, 3H, $COOCH_3$), 1.82 (q, *J*=6.6 Hz, 4H, 2× CH_2), 1.50 (q, *J*=6.6 Hz, 4H, 2× CH_2), 1.30 (br s, 16H, 8× CH_2), 0.90 (t, *J*=6.6 Hz, 6H, 3× CH_3); δ_C (125 MHz $CDCl_3$): 167.2, 162.5, 158.5, 157.4, 152.9, 145.7, 141.8, 139.6, 136.6, 135.2, 132.4, 131.9, 130.0, 129.3, 128.0, 127.4, 127.0, 126.3, 125.5, 124.1, 122.3, 115.5, 114.6, 114.0, 112.1, 71.4, 70.8, 50.6, 32.3, 31.8, 31.4, 30.6, 30.3, 29.9, 26.7, 26.4, 26.0, 23.1, 22.8, 14.4, 13.9; ν_{max}(KBr) 3486 (NH), 3195, 3104, 2961, 2935, 2855, 1708 (C=O_{ester}), 1675 (C=O_{amide}), 1634 (C=C), 1460, 1319, 1243 (C–O_{ester}), 885, 769, 663, 619 cm^{-1}; Anal. Calcd for $C_{49}H_{57}NO_5S$ (772.05): C, 76.23, H, 7.44, N, 1.81, S, 4.15%. Found: C, 76.40, H, 7.67, N, 1.88, S, 4.10%. Mass (ESI) *m*/*z* (%) 771.10.

4.9.5. 2-{4-[2-(4-Decyloxy-phenyl)-vinyl]-benzoylamino}-4-(4′-octyloxy-biphenyl-4-yl)-thiophene-3-carboxylic acid methyl ester ***10e***. Yield: 38% (456 mg), yellow solid; mp=144–148 °C; R_f (CH_2Cl_2) 0.67; δ_H (500 MHz $CDCl_3$): 12.35 (br s, 1H, NH), 8.01 (d, *J*=8.0 Hz, 2H), 7.85 (d, *J*=8.0 Hz, 2H), 7.56 (d, *J*=8.0 Hz, 2H), 7.52 (d, *J*=8.0 Hz, 2H), 7.46 (d, *J*=8.0 Hz, 2H), 7.38 (d, *J*=8.0 Hz, 2H), 7.16 (d, *J*=16.0 Hz, 1H), 7.00 (d, *J*=8.0 Hz, 2H), 6.98 (d, *J*=16.0 Hz, 1H), 6.90 (d, *J*=8.0 Hz, 2H), 6.69 (s, 1H, $H_{thiophene}$), 4.01 (t, *J*=6.2 Hz, 2H, CH_2), 3.98 (t, *J*=6.4 Hz, 2H, CH_2), 3.69 (s, 3H, $COOCH_3$), 1.80 (q, *J*=6.4 Hz, 4H, 2× CH_2), 1.45 (q, *J*=6.2 Hz, 4H, 2× CH_2), 1.28 (br s, 20H, 10× CH_2), 0.88 (t, *J*=6.2 Hz, 3H, CH_3), 0.86 (t, *J*=6.2 Hz, 3H, CH_3); δ_C (125 MHz $CDCl_3$): 166.4, 161.5, 157.9, 153.3, 151.7, 147.4, 146.2, 140.2, 138.6, 135.8, 133.2, 132.0, 130.3, 129.5, 128.4, 127.6, 127.2, 126.4, 126.1, 124.4, 123.3, 116.5, 114.8, 112.4, 111.7, 71.5, 69.9, 51.3, 32.6, 32.0, 31.8, 30.9, 30.6, 30.3, 30.1, 29.7, 27.1, 26.6, 26.4, 24.0, 23.6, 14.2, 14.0; ν_{max}(KBr) 3474 (NH), 3168, 3116, 2952, 2935, 2861, 1719 (C=O_{ester}), 1669 (C=O_{amide}), 1625 (C=C), 1458, 1342, 1249 (C–O_{ester}), 902, 794, 676, 604 cm^{-1}; Anal. Calcd for $C_{51}H_{61}NO_5S$ (800.10): C, 76.56, H, 7.68, N, 1.75, S, 4.01%. Found: C, 76.80, H, 7.90, N, 1.83, S, 4.05%. Mass (ESI) *m*/*z* (%) 799.89.

4.9.6. 2-{4-[2-(4-Dodecyloxy-phenyl)-vinyl]-benzoylamino}-4-(4′-octyloxy-biphenyl-4-yl)-thiophene-3-carboxylic acid methyl ester ***10f***. Yield: 35% (435 mg), yellow solid; mp=118–122 °C; R_f (CH_2Cl_2) 0.76; δ_H (500 MHz $CDCl_3$): 12.35 (br s, 1H, NH), 8.04 (d, *J*=8.1 Hz, 2H), 7.63 (d, *J*=8.0 Hz, 2H), 7.58 (d, *J*=8.0 Hz, 2H), 7.56 (d, *J*=8.0 Hz, 2H), 7.38 (d, *J*=8.0 Hz, 2H), 7.17 (d, *J*=16.2 Hz, 1H), 6.99 (d, *J*=8.0 Hz, 2H), 6.98 (d, *J*=8.1 Hz, 2H), 6.90 (d, *J*=16.2 Hz, 1H), 6.88 (d, *J*=8.0 Hz, 2H), 6.70 (s, 1H, $H_{tihophene}$), 4.06 (t, *J*=6.4 Hz, 2H, CH_2), 4.01 (t, *J*=6.4 Hz, 2H, CH_2), 3.70 (s, 3H, $COOCH_3$), 1.82 (q, *J*=6.4 Hz, 4H, 2× CH_2), 1.51 (q, *J*=6.4 Hz, 4H, 2× CH_2), 1.27 (br s, 24H, 12× CH_2), 0.90 (t, *J*=6.4 Hz, 3H, CH_3), 0.88 (t, *J*=6.4 Hz, 3H, CH_3); δ_C (125 MHz $CDCl_3$): 166.8, 163.0, 158.7, 153.2, 151.1, 148.1, 145.4, 139.6, 136.7, 135.7, 133.0, 132.4, 130.0, 129.7, 128.8, 128.4, 128.1, 127.5, 127.0, 126.4, 124.1, 123.0, 116.3, 115.0, 114.5, 112.1, 71.1, 70.9, 51.6, 32.6, 32.2, 31.8, 31.4, 31.0, 30.7, 29.8, 29.5, 27.0, 26.8, 26.5, 26.1, 23.8, 23.4, 14.4, 13.9; ν_{max}(KBr) 3460 (NH), 3152, 3098, 2944, 2920, 2845, 1706 (C=O_{ester}), 1671 (C=O_{amide}), 1634 (C=C), 1470, 1319, 1251 (C–O_{ester}), 908, 799, 685, 619 cm^{-1}; Anal. Calcd for $C_{53}H_{65}NO_5S$ (828.15): C, 76.87, H, 7.91, N, 1.69, S, 3.87%. Found: C, 77.05, H, 7.95, N, 1.72, S, 3.93%. Mass (ESI) *m*/*z* (%) 827.5.

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