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2-Methoxypyridine Derivatives: Synthesis, Liquid Crystalline and Photo-physical Properties

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Abstract: We herein report the design and synthesis of fourteen new bent shaped luminescent mesogens carrying a pyridine core substituted with various polar groups. They possess slightly non-planar bent conformation with various intermolecular interactions, as evidenced by their single crystal X-ray diffraction study and exhibit ambient to elevated temperature liquid crystalline phase (N or Col_r), which has been confirmed by differential scanning calorimetry, polarized optical microscopy, and powder X-ray diffraction techniques. In the compounds, nature of polar substituents influences significantly on the formation of mesophase over the wide thermal range. Appearance of nematic phase is due to the presence of lateral CN group attached to pyridine core and terminal F or Cl substituent. Formation of rectangular columnar phase is attributed to the absence of lateral CN group on pyridine core and the presence of terminal Br, NO_2 or 4-pyridyl group.

Keywords: 2-Methoxypyridine / 2-Methoxy-3-cyanopyridine / Crystal Structure / Liquid Crystal / Optical Properties.

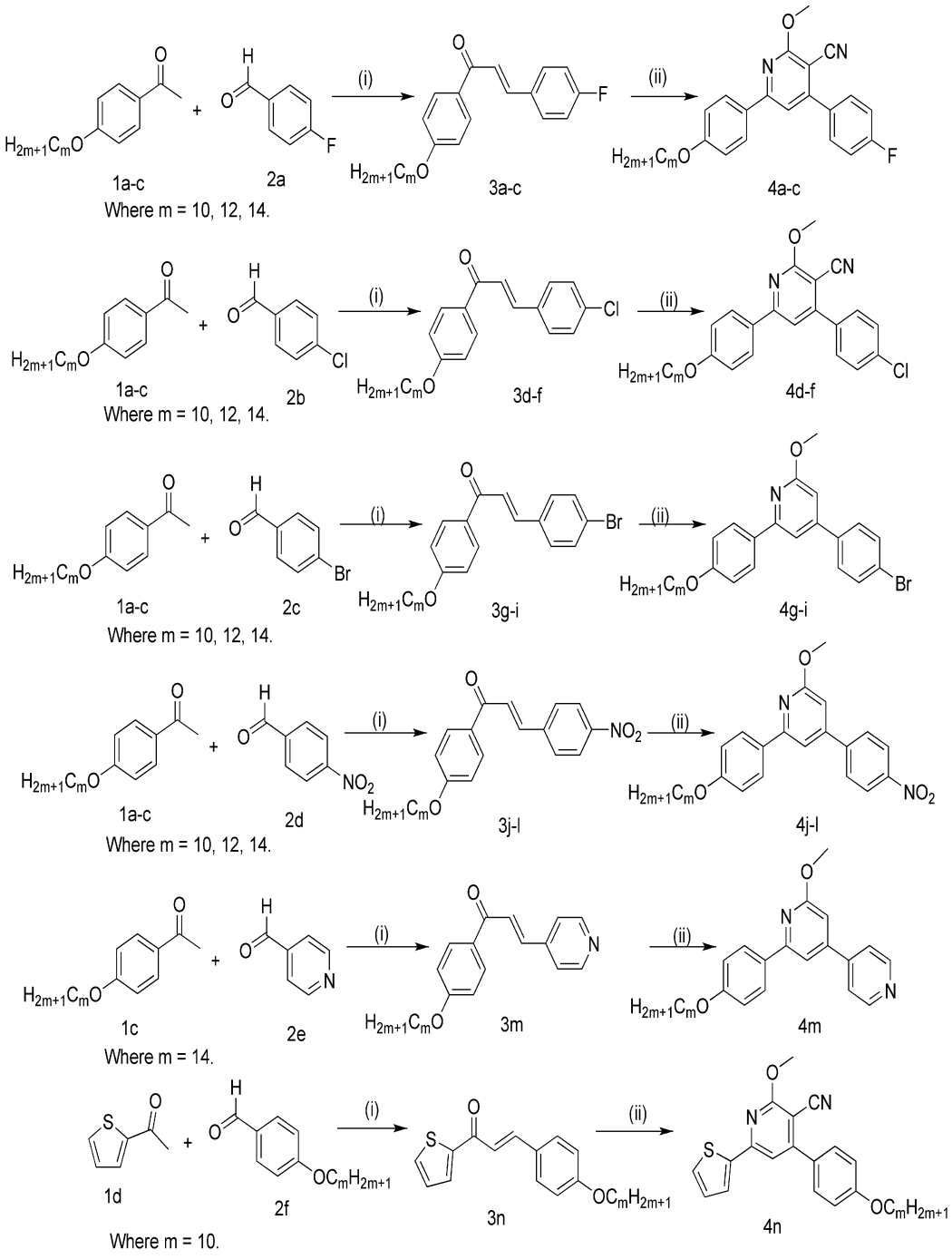
Introduction

Presently, organic mesogens with luminescent properties are under intense investigation because of their wide applicability in the field of LEDs (light-emitting diodes), TFTs (thin-film transistors), solar cells, solid lasers and photovoltaic devices.[1-5] Because of the fact that the self-organized luminescent organic materials are capable of showing excellent charge carrier mobilities and easy processability, they contribute significantly in improving the device

performance.[6] In view of this, many organic molecules were designed and synthesized as potential luminescent mesogens for applications in opto-electronic devices. Amongst them, heterocyclic compounds[7-11] play an important role, as they are capable of showing complex liquid crystalline behavior due to the presence of polarizable heteroatom in the aromatic ring. Eventually, several substituted pyridines were reported to be good liquid crystalline materials, as pyridine skeleton has been found to be an excellent electron deficient heterocycle with unique properties such as rigid structure, ability to form complex liquid crystalline phase, luminescence efficiency, charge carrier ability, thermal and photochemical stability.[12, 13]

In the quest of novel pyridine based luminescent mesogens,[14-16] we thought of designing new molecules carrying 2-methoxypyridine or 2-methoxy-3-cyanopyridine as a core and suitably substituted aryl/heteroaryl system at position-4 as well as variable alkoxyaryl group at position-6 of the core moiety as terminal systems, with possible three ring bent shaped structure. In the design, pyridine was selected as a core because of its ability to form mesogenic phase through intermolecular interactions and its rigid structure with an excellent electron transporting nature as well as good photophysical properties.[17-19] In addition, a polar substituent like F, Cl, Br, NO_2, 4-pyridyl, 2-thiophenyl group was introduced at appropriate position in order to induce complex mesogenic behavior while variable alkoxy chain (m = 10, 12 and 14) was incorporated as terminal substituent to attain ambient temperature liquid crystalline behavior.

Accordingly, we designed new 4,6-disubstituted-3-cyanopyridines (**4a-f** and **4n**) and 4,6-disubstituted-2-methoxypyridines (**4g-m**), with the hope that new molecules would emerge as blue emissive liquid crystalline materials with good electron transporting property. Newly designed molecules were synthesized through simple synthetic routes and their structures were established using spectral techniques. Their mesogenic property was investigated using polarized optical microscopy (POM), differential scanning calorimetry (DSC) and powder X-ray diffraction (PXRD) methods. Further, their photophysical properties were studied by UV-visible absorption and fluorescence emission spectroscopy. Finally, their crystal structure, shape and intermolecular interactions were determined following single crystal X-ray diffraction (SCXRD) analysis. The experimental results were discussed and the effect of substituents on the observed mesogenic as well as photophysical properties was established.



Scheme 1. Reagents and conditions: (i) KOH/EtOH, rt; (ii) Malononitrile, NaOMe, MeOH, rt.

Table 1 Crystal data and structure refinement for compounds **4m** and **4n**.

Compound	**4m**	**4n**
Chemical formula	$C_{31}H_{42}N_2O_2$	$C_{48}H_{51}N_4S_2$
Formula mass	474.67	812.07
Crystal system	Triclinic	Orthorhombic
Space group	*P-1*	*Aba2*
a (Å)	7.3355 (5)	14.8343(5)
b (Å)	9.7607 (7)	44.690(2)
c (Å)	19.5372 (14)	7.3614(3)
α (°)	97.873 (5)	90.00
β (°)	94.801 (4)	90.00
γ (°)	104.460 (4)	90.00
Unit cell volume (Å^3)	1331.60 (16)	4880.2 (3)
Z	2	4
Temperature (K)	296	100
ρ_{calc} (g cm^{-3})	1.184	1.194
Absorption coefficient (mm^{-1})	0.07	0.15
F(000)	516.0	1753
Crystal size (mm^3)	0.29 x 0.26 x 0.25	0.35 x 0.26 x 0.21
No. of reflections measured	16730	12948
No. of independent reflections	4704	4301
R_{int}	0.052	0.059
$\Delta\rho$min,max (e Å^{-3})	-0.33, 0.28	-0.47, 1.20
Final R_1 values (I>2σ(I))	0.0588	0.0844
Final $wR(F^2)$ values (I>2σ(I))	0.1533	0.2353
Final R_1 values (all data)	0.1121	0.1039
Final $wR(F^2)$ values (all data)	0.174	0.2599
GOOF	0.99	1.06
CCDC	978127	978451

Results and Discussion

Synthesis and structure characterization

The synthetic route for compounds **4a-n** is shown in Scheme 1. Compounds **1a-c** were prepared by O-alkylation of 4-hydroxyacetophenone with various alkyl bromides (*i.e.* m=10, 12 and 14) as per reported procedure.[20] Similarly, compound **2f** was prepared by O-alkylation of 4-hydroxybenzaldehyde with 1-bromodecane in good yield following the reported procedure.[21] The intermediate prop-2-en-1-ones **3a-n** were prepared from substituted ketones **1a-d** and aldehydes **2a-f** using Claisen – Schmidth reaction. Finally, they were cyclized to obtain final compounds **4a-n** by reacting them with malononitrile in presence of sodium methoxide. The purified compounds were characterized by FTIR, NMR as well as mass spectral methods and their analytical purity was checked by elemental analysis. Generally, the chalcone derivatives upon reaction with malononitrile in presence of sodium methoxide lead to form 2-methoxy-3-cyanopyridines.[22,23] Interestingly, in the present work the final step yielded two different substituted pyridines, *viz.* 2-methoxy-3-cyanopyridine (**4a-f** and **4n**) and 2-methoxypyridine (**4g-m**). Here, the formation of unexpected 2-methoxypyridine (**4g-m**) is mainly attributed to the presence of electron withdrawing substituents, *viz.* 4-nitrophenyl, 4-pyridyl, 4-bromophenyl attached to prop-2-en-1-ones **3g-m**, which facilitates the dehydrocyanation rather than dehydrogenation. The crystal structure analysis of compounds **4m** and **4n** evidences the formation of two different cyclized products.

In FTIR spectrum, compound (**4a-f** and **4n**) shows two strong IR bands at about 2920 and 2850 cm^{-1} that correspond to methylene asymmetrical and symmetrical C-H stretching vibrations. Further, appearance of a strong IR band at around 2220 cm^{-1} indicates the presence of CN group in the structure. In addition, appearance of a strong peak at about 1580 cm^{-1} due to ring C=N stretching vibrations, has confirmed the effective formation of 2-methoxy-3-cyanopyridine via cyclization. However, in FTIR spectrum of compound (**4g-m**), stretching vibrations of C-H and C=N groups have appeared as strong peaks at about 2913-2850 cm^{-1} and 1577-1570 cm^{-1}, respectively and the peak due to CN at around 2220 cm^{-1} remains absent, which confirms the formation of 2-methoxy pyridine (**4g-m**).

In ^{1}H NMR spectrum of compound (**4a-f** and **4n)**, aromatic protons have resonated in the range of δ 8.07-7.03 ppm and protons of position-4 of pyridine ring have appeared as singlet at about δ 7.38 ppm. In addition, three protons of methoxy substituent at position-2 of pyridine ring resonate at around δ 4.22 ppm as a singlet, confirming the effective construction of 2-methoxy-3-cyanopyridine from prop-2-en-1-one. Further, the appearance of primary and secondary proton signals in the range of δ 1.86-1.00 ppm has established the presence of terminal alkoxy chain in the compounds. Further, the ^{1}H NMR spectrum of compound (**4g-m**) displays an additional singlet at about δ 6.80 ppm when compared to ^{1}H NMR spectrum of compound (**4a-f** and **4n**), evidencing the cyclization through dehydrocyanation. The appearance of additional singlet is due to the presence of proton attached to position-3 of pyridine ring.

Crystal structure of compound 4m

In general, it is difficult to grow superior quality crystals of a mesogenic compound carrying flexible alkoxy chains. In spite, we could obtain high-quality colorless block shaped crystals of compound **4m** by slow evaporation of solution (chloroform and methanol in 1:1 ratio). Its crystal structure was determined by SCXRD analysis. The molecular structure with the atom-numbering scheme and packing of compound **4m** are shown in Figures 1 and 2, respectively. Crystal data of compound **4m** are tabulated in Table 1. The selected bond lengths and bond angles are given in Table S1 (SI). The study reveals that **4m** crystallizes in triclinic space group *P*-1 with cell parameters are a=7.3355 (5) Å, b=9.7607 (7) Å, c =19.5372 (14) Å, V=4880.2(3) Å^{3}, Z=2. From the X-ray analysis data, it is evident that the molecule is not planar and but, distorted. Interestingly, 4-pyridyl ring substituted at position-4 of central pyridine ring makes a torsion angle χ[C(26), C(3), C(4), C(27)] of 37.6° (4), while the 4-tetradecyloxyphenyl ring substituted at its position-6, forms a torsion angle of χ[C(8), C(7), C(6), N(2)] of 4.2° (3), which is less than the previous one. The two ring systems having least torsion angle construct nearly a plane, providing a large conjugated system within the molecule. Further, the results reveal that the carbon-carbon bond lengths on the molecular skeleton are basically intermediate between typical C-C single (1.54 Å) and C=C double (1.34 Å) bonds. The carbon-nitrogen bond lengths are also intermediate between typical C-N single (1.47 Å) and C=N double (1.27 Å) bonds. The carbon-oxygen bond lengths directly attached to aromatic systems are also intermediate between that of

C-O single (1.43 Å) and C=O double (1.24 Å) bonds. This confirms the delocalization of π-electrons of 4-tetradecyloxyphenyl and pyridine systems, which in turn promotes the electron-donating tendency of alkoxy group.

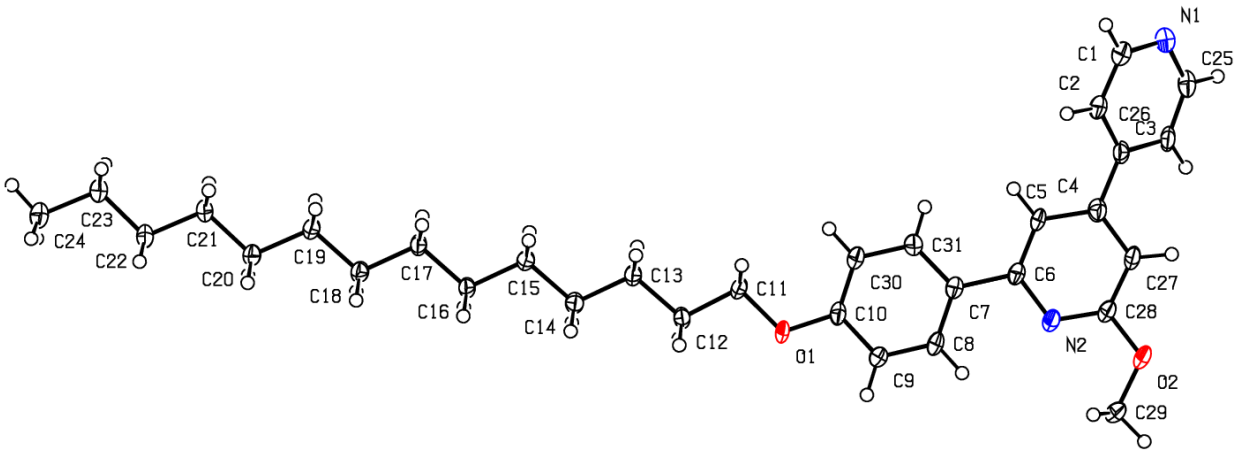


Figure 1. The molecular structure with atom-numbering scheme of compound **4m** (Hydrogen atoms are omitted from the structure for clarity).

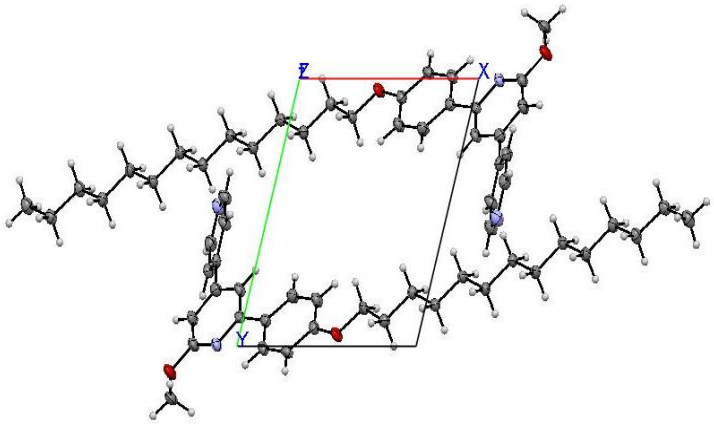


Figure 2. The molecular packing of compound **4m**, viewed along c-axis.

Crystal structure of compound 4n

High-quality colorless block shaped crystals of compound **4n** were obtained by slow evaporation of solution (chloroform and methanol in 1:1 ratio). The SCXRD experiment was carried out at 100 K and the obtained crystal data are presented in Table 1. The molecular structure with the

atom-numbering scheme and packing of compound **4n** are shown in Figures 3 and 4, respectively. The selected bond lengths and angles are given in Table S2 (SI). Single crystal study reveals that **4n** crystallizes in Orthorhombic space group *Aba2* with cell parameters are a= 14.8343(5) Å, b= 44.690(2) Å, c = 7.3614(3) Å, V= 4880.2(3) $Å^3$, Z= 8. From the X-ray analysis data, it is evident that the molecule is not planar and but slightly distorted. Interestingly, 4-decyloxyphenyl ring substituted at position-4 of central pyridine ring makes a torsion angle χ[C(27), C(8), C(3), C(16)] of -41.9° (6), while the 2-thiophenyl ring substituted at its position-6, forms a torsion angle of χ[C(4), C(2), C(18), C(27)] of -4.4° (8). Thus, the two ring systems having the least torsion angle construct nearly a plane, providing a large conjugated system within the molecule. Further, the results reveals that the measured bond length values of carbon-carbon, carbon-oxygen and carbon-nitrogen atoms possess partial double bond character. This observation clearly evidences the delocalization of π-electrons of thiophenyl and pyridine systems.

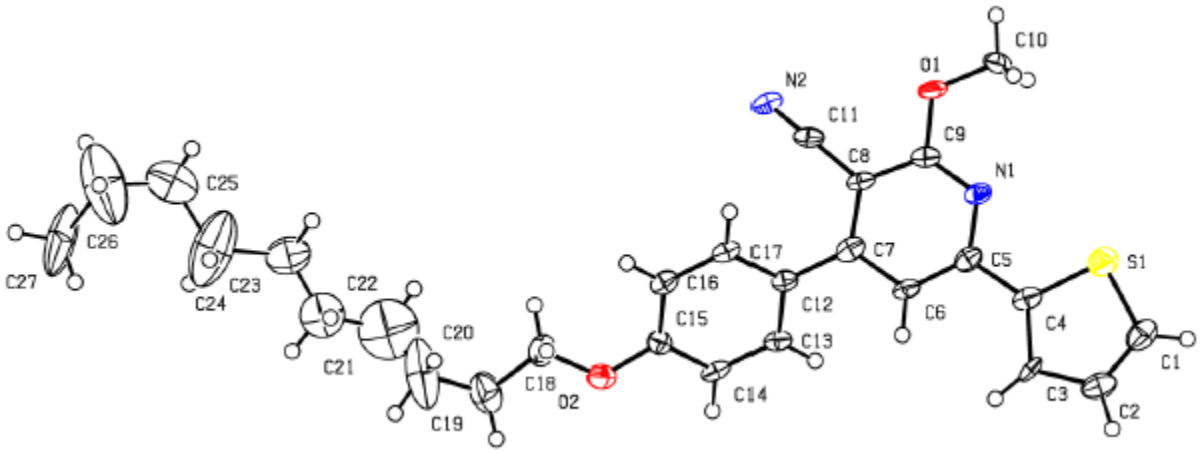


Figure 3. The molecular structure with atom-numbering scheme of compound **4n** (Hydrogen atoms are omitted from the structure for clarity).

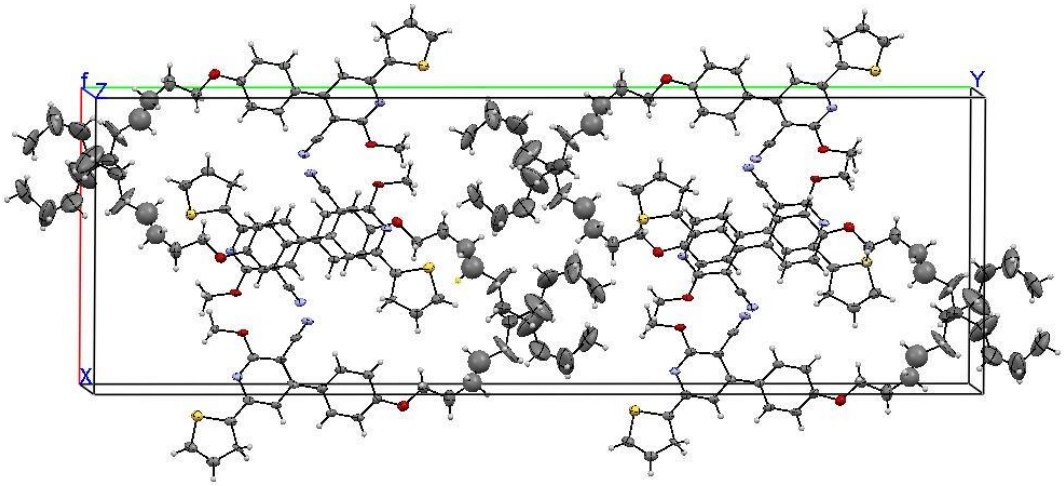


Figure 4. The molecular packing of compound **4n**.

Mesomorphic behavior

The transition temperature and phase assignment of compounds **4a-n** were determined by POM and DSC studies. Their results are summarized in Table 2. Among them, compounds **4a-m** show liquid crystal to isotropic transition, while compound **4n** exhibits only crystalline to isotropic transition. Interestingly, compounds bearing 2-methoxy-3-cyanopyridine as central core shows nematic phase except **4n**, while compounds carrying 2-methoxypyridine as central core display columnar phase. In structures of **4a-c**, the appearance of nematic phase (Figure 5(a)) is mainly attributed to the presence of polar 4-flurophenyl at position-4 and alkoxyphenyl (m=10, 12 and 14) at position-6 of 2-methoxy-3-cyanopyridine core. Similarly, compounds **4d-f** carrying polar 4-chlorophenyl substituent exhibit nematic phase. The appearance of nematic phase in them is due to the presence of polar 4-chlorophenyl moiety at position-4 and alkoxyphenyl (m=10, 12 and 14) group at position-6 of 2-methoxy-3-cyanopyridine core. To sum up, in compounds **4a-f**, the presence of lateral highly polar CN group and terminal F or Cl functional group are responsible for exhibiting nematic phase.

The liquid crystalline phases of compounds **4g-m** show well defined fan-shaped texture appeared as rectangular columnar phase (Col_r). The rectangular columnar phase of **4h**, **4i** and **4m** are shown in Figures 5(b-d), respectively. In case of compounds **4g-i**, the appearance of Col_r is mainly attributed to presence of 4-bromophenyl moiety at position-4 and alkoxyphenyl (m=10,

12 and 14) group at position-6 of 2-methoxypyridine core. Here, the favorable structural feature facilitates to form dipole-dipole interaction between the molecules, which may be one of the reasons for the formation of Col_r phase. Further, these compounds show wide range of Col_r phase from ambient temperature to 114 °C, at both the heating and the cooling cycle. Furthermore, the non-aligned compound **4i** was subjected to PXRD measurements at 35 °C. The obtained pattern was subjected to peak indexing analysis and the peaks are being indexed to a Col_r phase (Figure 6) with symmetry *P2/a* (lattice constants: a=38.76 Å, b=26.66 Å (Table 3). In the small angle region, the observed d-spacing values 21.97, 19.38 and 15.67 can be indexed to (11), (20) and (21) planes. A small as well as a broad peak corresponding to the stacking periodicity of a columnar structure (ca. 4.26 and 3.63 Å) was observed. This observation is indicative of disordering of the molecular stacking.

Similarly, the compounds **4j-l** exhibit Col_r phase at higher temperature ranging from 100 to 140 °C. The appearance of Col_r phase is due to dimerization of molecules caused by the presence of terminal 4-nitrophenyl group at position-4 of 2-methoxypyridine unit as well as variation of other terminal 4-alkoxyphenyl group (m=10, 12 or 14) at position-6. The unfavorable overlapping of the aromatic and aliphatic segments as well as dimerization of molecules facilitates the formation of columnar phase in bent shaped compounds (**4j-l)**.[24] Notably, Col_r mesophase range in these compounds was found to be nearly 40 °C even though it carries a nitro functionality as a highly polarizable group. Generally, it is expected that nitro functionality provides a wide range of mesophase, but the obtained mesophase range is very much less than that of **4g-i**. This observation is due to the presence of terminal polar planar nitro group that believed to promote crystallization. Because of enhanced crystallization, compounds **4j-l** exhibit Col_r phase at high melting temperature as well as decreased mesophase.

Also, the compound **4m** exhibits Col_r phase from ambient to 94 °C. Appearance of Col_r phase is attributed to the presence of 4-pyridyl group at position-4 and 4-tetradecyloxyphenyl functionality at position-6 of 2-methoxypyridine core. In addition, PXRD measurements of the non-aligned sample **4m** at 35 °C gives a pattern that is characteristic of a Col_r phase with symmetry C_{2mm} (lattice constants: a=31.04 Å, b=25.08 Å; Table 3). In the small angle region, the observed *d*-spacing values 19.51, 15.52 and 9.51 Å can be indexed to (11), (20) and (22) planes.

Also, only reflections $h+k=2n$ have been observed in the small angle region and thus, reflections can be assigned to a centered rectangular lattice (C_{2mm}). A small and broad peak corresponding to the stacking periodicity of a columnar structure (ca. 4.50 and 3.75 Å) was seen. This observation is indicative of disordering of the molecular stacking. Nevertheless, the compound **4n**, was unable to exhibit any kind of liquid crystal transitions even though it possesses 2-thiophenyl ring at position-6 as well as 4-decyloxyphenyl group at position-4 of 2-methoxy-3-cyanopyridine core. Further, it is established that the compounds with short intermolecular core-to-core distance favors the high charge-carrier mobilities along the columns.[25] Hence, a better charge-carrier mobility along the columns is expected for compounds **4g-i** and **4m** since the observed distance of ~3.70 Å is comparable to that of the semiconducting columnar mesogens reported in the literature.[26]

Table 2 Phase transition data of compounds **4a-n**

Compounds	m	Terminal substituent	Transition	Temperature/ ^{o}C	ΔH/kJ mol^{-1}
4a	10	F	Cr –N	115.7	21.0
			N-I	128.3	0.8
4b	12	F	Cr-N	109.6	20.0
			N-I	128.7	1.3
4c	14	F	Cr-N	101.4	18.9
			N-I	125.3	1.4
4d	10	Cl	Cr-N	117.9	22.0
			N-I	133.7	0.6
4e	12	Cl	Cr-N	109	20.9
			N-I	128.2	1.1
4f	14	Cl	Cr-N	122.2	24.1
			N-I	138.8	1.4
4g	10	Br	Col_r-I	107.2	4.8
4h	12	Br	Col_r-I	113.6	5.1
4i	14	Br	Col_r-I	90.84	6.4
4j	10	NO_2	Cr-Col_r	100.9	8.6

			Col_r-I	114.9	3.7
4k	12	NO_2	Cr-Col_r	129.2	15.1
			Col_r-I	137.8	3.6
4l	14	NO_2	Cr-Col_r	104.7	14.8
			Col_r-I	117.9	4.7
4m	14	4-pyridinyl	Col_r-I	93.7	8.8
4n	10	2-thiophenyl	Cr-I	98.6	28.6

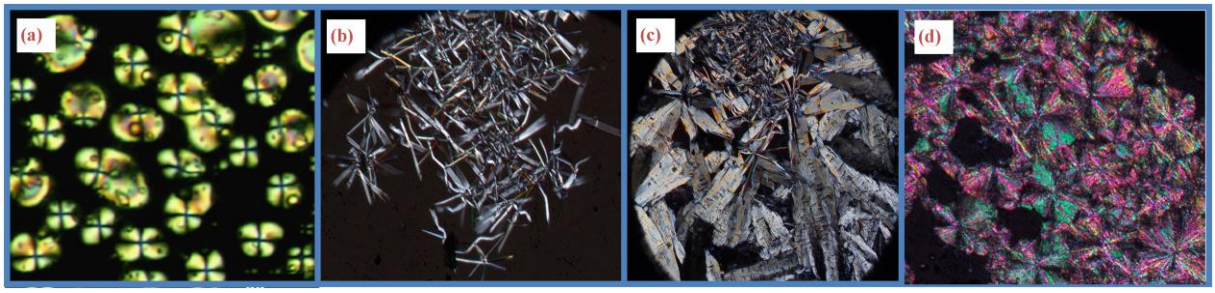


Figure 5. Photomicrographs (a) nematic phase of **4c** at 105 °C; (b) columnar phase of **4h** at 110 °C (c) columnar phase of **4i** at 88 °C; (d) columnar phase of **4m** at 35 °C.

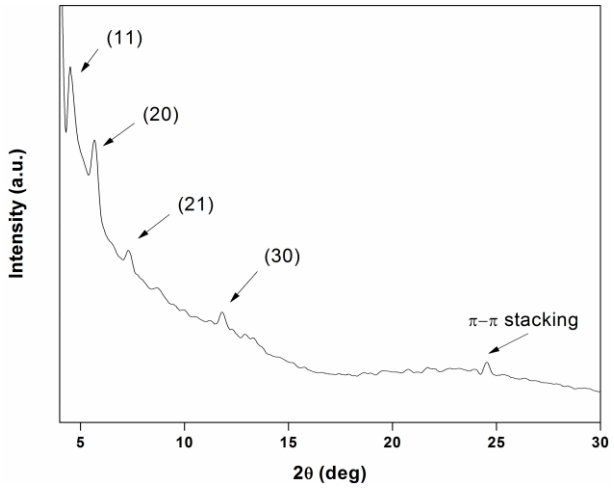


Figure 6**.** Powder X-ray diffraction pattern of **4i** at 35°C.

Table 3 X-ray diffraction results of **4i** and **4m** in their rectangular columnar phase

Compound	d_{obs}/Å	Phase and Symmetry	*hk*	d_{cal}/Å	Parameters
	21.97	Col_r	*11*	*21.97*	*T= 35 °C*
	19.38	*P2/a*	*20*	*19.38*	*a= 38.76 Å*
	15.67		*21*	*15.67*	*b=26.66 Å*
	12.62		*30*	*12.92*	*S= 1033.34 Å²*
4i	*4.26*		*halo (h)*		*V_m=924.41 Å³*
	3.63		*π-π stacking*		*S_{col}=516.67 Å²*
	19.51	Col_r	*11*	*19.51*	*T= 35 °C*
	15.52	*C_{2mm}*	*20*	*15.52*	*a= 31.04 Å*
	9.51		*22*	*9.70*	*b=25.08 Å*
4m	*4.50*		*halo (h)*		*S= 778.48 Å²*
	3.75		*π-π stacking*		*V_m=794.10 Å³*
					S_{col}=395.53 Å²

Note: d_{obs} and d_{cal} are the measured and theoretical diffraction spacings; d_{cal} is deduced from the following mathematical expression: $1/d_{hk} = \sqrt{(h^2/a^2+k^2/b^2)}$; *hk* are the indexations of the reflections corresponding to the rectangular symmetry, and *a* and *b* are the lattice parameters of the Col_r phase ($a=2d_{20}$). For the Col_r, S=a×b where S is the lattice area and $S_{col}=S/2$ where, S_{col} is the columnar cross-section. Molecular volume V_m is calculated using the formula $V_m=M / \lambda\delta N_A$, where *M* is the molecular weight of the compound, N_A is the Avogadro number, δ is the volume mass density (≈1g cm^{-3}), and $\lambda(T)$ is a temperature correction coefficient at the temperature of the experiment *(T)*, $\lambda=V_{CH2}(T_0)/V_{CH2}(T)$, where $T_0=25$ °C, $V_{CH2}(T)=26.5616+0.02023T$.

Optical properties

The UV-visible absorption spectra of compounds **4a-n** were recorded using chloroform as a solvent at the concentration of 10^{-5} M and the results are tabulated in Table 4. The spectra of representative compounds **4a,d,g,j,m,n** are shown in Figure 7. The results reveal that the compounds show a strong absorption band (λ_{abs}) in the range of 330-350 nm, which has been

assigned to π-π* electronic transition occurring in their conjugated structure. The observed λ_{abs} values mainly depend on the nature of substituents present in them. Amongst **4a-n**, compounds **4j-l** display the highest λ_{abs} at about 348 nm. This is due to the presence of highly electron withdrawing NO_2 group that has caused increase in electron drift from electron-donating alkoxy group to it through π-conjugated system. While the compounds carrying F, Cl or Br substituent show λ_{abs} at around 341 nm, which is due to the relatively less electron withdrawing nature of the substituents. Further, compound **4n** bearing electron donating decyloxyphenyl and thiophene ring with electron withdrawing 2-methoxy-3-cyanopyridine system displays a strong absorption band at 344 nm, supporting its donor-acceptor-donor model. However, the variation of alkoxy chain length [*i.e*. m=10, 12 or 14] has not influenced their absorption band.

Table 4 Optical characteristics of compounds **4a-n**

Compound	**λ_{abs} (solution) /nm**	**λ_{em} (solution) /nm**	**Φ_f (solution) /%**	**λ_{em} (film) /nm**
4a	339	397	62.2	431
4b	339	398	52.3	433
4c	340	397	57.1	433
4d	340	402	60.2	414
4e	341	402	65.2	416
4f	341	402	58.3	415
4g	342	404	66.5	422
4h	342	402	60.3	424
4i	342	402	60.6	425
4j	347	411	61.4	469
4k	348	415	73.7	470
4l	347	414	71.7	470
4m	327	409	67.3	441
4n	344	397	47.0	408

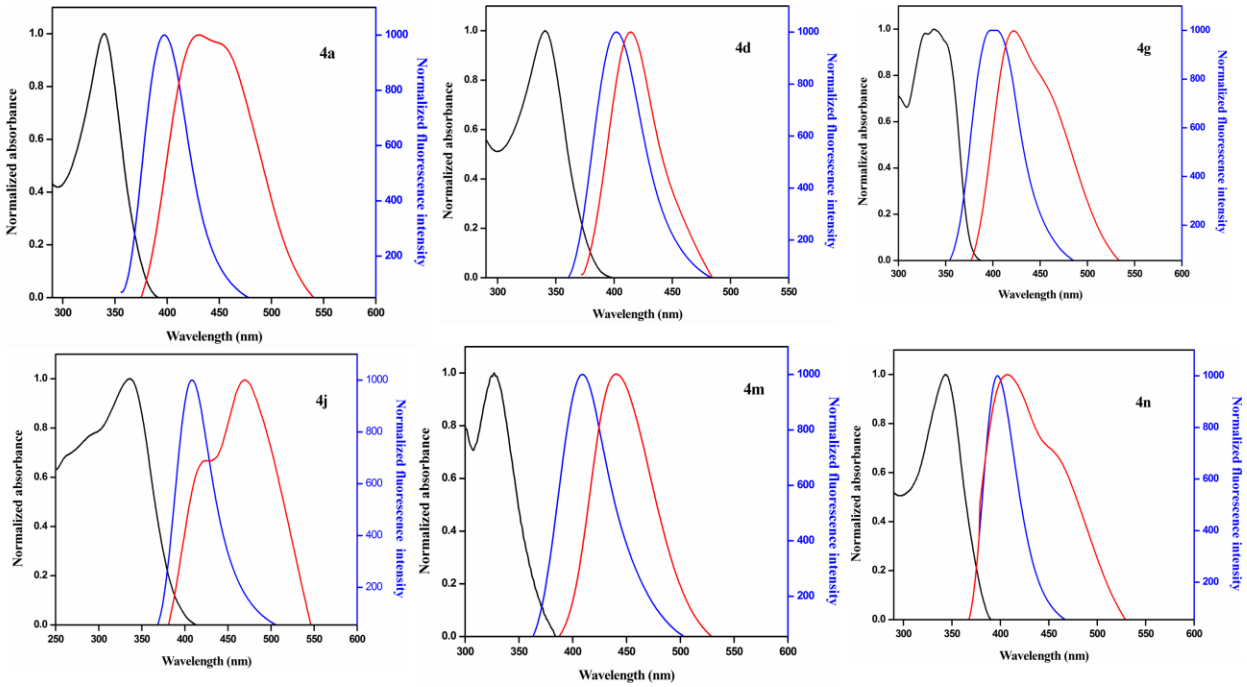


Figure 7. Photophysical properties of compounds **4a,d,g,j,m,n** (black line-absorption band in solution; blue and red line- emission bands in solution and film states, respectively)

The fluorescence emission spectra of compounds **4a-n** were recorded both in solution and film state at room temperature. The required thin films were prepared over the glass slide by spin coating the solution of compounds in chloroform. The spectra of representative compounds **4a,d,g,j,m,n** are given in Figure 7. The compounds show blue emission band in the range of 397-418 nm (excitation wavelength of 330 nm) in solution state with relative quantum yield of about 45-75 % when compared to that of quinine sulphate (Φ_f = 54 %).[27] Their results are summarized in Table 4. From the results, it is clear that as the strength of polar substituent increases, emission band shifts to higher wavelengths. Hence, the compounds **4j-l** with polar substituent, *i.e.* NO_2 show 15-20 nm red shifts when compared to the compounds with less polar substituent (*i.e.* F, Cl or Br). However, variation in terminal alkoxy chain length has negligible effect on their emission band. In addition, the compounds exhibit blue emission band in the range of 414-470 nm in their film state. Here, the emission bands have red shifted by about 15-60 nm when compared to the values obtained in their solution state. The observed red shifts are due to the intimate overlap of molecular cores in their film state. Thus, the target compounds have emerged as good blue emissive materials for optoelectronic device applications.

Conclusion

Fourteen new blue luminescent mesogens (**4a-n**) carrying 2-methoxy-3-cyanopyridine or 2-methoxypyridine unit as a core and variable alkoxy phenyl as well as substituted aryl/heteroaryl rings as terminal substituents were successfully synthesized and characterized. Compounds **4g-i** and **4m** show stable room temperature columnar phase with good charge-carrier mobility due to the presence of shorter intermolecular core-to-core distance. While compounds **4a-f** and **4j-l** exhibit either nematic phase or columnar phase at slightly elevated temperature depending on the nature of core and terminal substituents. Their photophysical study indicates that the compounds are promising blue emissive materials and the observed optical properties are sensitive to the polar substituents. The single crystal study reveals that compounds **4a-n** possess a bent-shaped structure with slightly non-planar arrangement and various intermolecular interactions. Conclusively, the molecules have emerged as good charge transporting blue emissive mesogens for applications in optoelectronic devices.

Experimental Section

General

All the reagents and organic solvents were used as received from commercial sources. All the compounds were purified by crystallization from analytical grade solvents. The purity of sample was confirmed by thin layer chromatography (Merck 60 Kieselgel F 254). IR spectra were recorded on a Nicolet Avatar 5700 FTIR (Thermo Electron Corporation); the spectral positions are given in wavenumber (cm^{-1}) units. The UV-visible and photoluminescence spectra were recorded by GBC Cintra 101 (wavelength range: 250-700 nm) and Perkin Elmer LS55 fluorescence spectrophotometers (wavelength range: 300-700 nm), respectively. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker Avance DPX spectrometer at RT using $CDCl_3$ as solvent. The chemical shifts are reported in parts per million relative to TMS as an internal standard. Coupling constants are expressed in hertz. Mass spectra (ESI) were recorded on Waters ZQ-4000 liquid chromatography-mass spectrometer. Elemental analyses were carried out on a Flash EA1112 analyzer (Thermo Electron Corporation).

Thermal behavior and liquid crystalline property of **4a-n** were studied by using a Leitz Ortholux II Pol-BK microscope equipped with a Mettler FP82HT hot stage. Clean glass slides were used to examine the liquid crystalline property of the samples. The transition temperatures and associated enthalpies were determined by using a SHIMADZU DSC-60 differential scanning calorimeter with a heating rate of 10 $^{\circ}$C min^{-1} (the apparatus was calibrated with indium, 156.6 $^{\circ}$C). Peak temperatures in the DSC traces due to phase transitions of the samples were found to be in agreement with those of the optical experimentsX-ray diffraction (XRD) studies were carried out on powder samples in Lindemann capillaries with CuKα radiation using an Image Plate Detector (MAC Science, Japan) equipped with double mirror focusing optics.

Single crystals of **4m** and **4n** suitable for single crystal X-ray structure determination were obtained by recrystallization from the chloroform/methanol mixture at room temperature. A crystal of suitable size was mounted using a Mitigen micromount and data collection was done on a Bruker Smart X2S bench top diffractometer equipped with a micro-focus MoKα radiation (λ =0.71073) at 293 K.[28] The machine was operated at 50kV and 1mA. Data reduction was performed using SAINTPLUS. Scaling, absorption correction was done using SADABS, all embedded in the Apex2 software suite.[28] The crystal structure was solved by direct methods using XS and the structure refinement was done using XL in the SHELXTL package.[29] The position and thermal parameters of all the non-hydrogen atoms were refined. The hydrogen's were fixed in geometrically calculated positions and refined isotropically. The ORTEP diagrams and packing diagrams were created using Mercury 3.0 and POV ray.

General procedure for synthesis of chalcone derivatives (3a-n)

The respective keto compounds **1a-d** (1 equivalent) and aldehyde compounds **2a-d** (1 equivalent) was taken in ethanol. To this added aqueous solution of potassium hydroxide (1.2 equivalents). Reaction mixture was stirred at room temperature for 4 h. The precipitated product was filtered. The crude product was purified by recrystallization from ethanol.

1-(4-(Decyloxy)phenyl)-3-(4-fluorophenyl)prop-2-en-1-one (3a). Yield: 1.2 g (78 %), m.p. 91-92 °C. FTIR (cm^{-1}): 2918, 2853, 1654, 1592, 1215, 1014, 817. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.02 (d, *J*=8 Hz, 2H, Ar-H) 7.78 (d, *J*=15.5 Hz, 1H, Olefinic-H), 7.66-7.64 (m, 2H, Ar-

H), 7.49 (d, *J*=15.5 Hz, 1H, Olefinic-H), 7.12 (d, *J*=8.7 Hz, 2H, Ar-H), 6.95 (d, *J*=8 Hz, 2H, Ar-H), 4.06 (t, *J*=6.5 Hz, 2H, -OCH_2-),1.85-1.82 (m, 2H, -OCH_2CH_2-), 1.49-1.29 (m, 14H, -CH_2-), 0.90 (t, *J*=6.5 Hz, 3H, -CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 188.4, 165.1, 163.1, 162.6, 142.5, 131.4, 131.3, 130.8, 130.7, 130.2, 130.1, 121.6, 116.1, 115.9, 114.3, 68.3, 31.9, 29.5, 29.3, 29.1, 26.0, 22.6, 14.1. MS (m/z): 383.2 $(M+H)^+$. Anal. Calcd. For. $C_{25}H_{31}FO_2$: C. 78.50; H. 8.17; Found: C. 78.79; H. 8.12.

1-(4-(Dodecyloxy)phenyl)-3-(4-fluorophenyl)prop-2-en-1-one (3b). Yield: 0.8 g (81 %), m.p. 88-89 °C. FTIR (cm^{-1}): 2913, 2848, 1655, 1596, 1250, 1015, 824. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.04 (d, *J*=9 Hz, 2H, Ar-H) 7.83 (d, *J*=15.5 Hz, 1H, Olefinic-H), 7.66-7.64 (m, 2H, Ar-H), 7.49 (d, *J*=15.5 Hz, 1H, Olefinic-H), 7.13 (t, *J*=8.7 Hz, 2H, Ar-H), 6.99 (d, *J*=9 Hz, 2H, Ar-H), 4.06 (t, *J*=6.5 Hz, 2H, -OCH_2-), 1.85-1.82 (m, 2H, -OCH_2CH_2-), 1.49-1.29 (m, 18H, -CH_2-), 0.90 (t, *J*=6.5 Hz, 3H, -CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 188.4, 165.1, 163.1, 162.6, 142.5, 131.4, 131.3, 130.8, 130.7, 130.2, 130.1, 121.6, 116.1, 115.9, 114.3, 68.3, 31.9, 29.5, 29.3, 29.1, 26.0, 22.6, 14.1. MS (m/z): 411.3 $(M+H)^+$. Anal. Calcd. For. $C_{27}H_{35}FO_2$: C. 78.99; H. 8.59; Found: C. 78.67; H. 8.66.

3-(4-Fluorophenyl)-1-(4-(tetradecyloxy)phenyl)prop-2-en-1-one (3c). Yield: 1.5 g (74 %), m.p. 96-97.5 °C. FTIR (cm^{-1}): 2913, 2847, 1655, 1597, 1250, 1016, 826. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.04 (d, *J*=9 Hz, 2H, Ar-H), 7.78 (d, *J*=15.5 Hz, 1H, Olefinic-H), 7.66-7.64 (m, 2H, Ar-H), 7.49 (d, *J*=15.5 Hz, 1H, Olefinic-H), 7.12 (t, *J*=8.5 Hz, 2H, Ar-H), 6.99 (d, *J*=8.5 Hz, 2H, Ar-H), 4.06 (t, *J*=6.5 Hz, 2H, -OCH_2-), 1.86-1.81 (m, 2H, -OCH_2CH_2-), 1.50-1.28 (m, 22H, -CH_2-), 0.90 (t, *J*=6.5 Hz, 3H, -CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 188.4, 165.1, 163.1, 162.6, 142.5, 131.4, 131.3, 130.8, 130.7, 130.2, 130.1, 121.6, 116.1, 115.9, 114.3, 68.3, 31.9, 29.5, 29.3, 29.1, 26.0, 22.6, 14.1. MS (m/z): 439.3 $(M+H)^+$. Anal. Calcd. For. $C_{29}H_{39}FO_2$: C. 79.41; H. 8.96; Found: C. 79.65; H. 8.88.

3-(4-Chlorophenyl)-1-(4-(decyloxy)phenyl)prop-2-en-1-one (3d). Yield: 1.3 g (75 %), m.p. 112-113 °C. FTIR (cm^{-1}): 2919, 2852, 1653, 1594, 1266, 1164, 1013, 812. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.04 (d, *J*=8.5 Hz, 2H, Ar-H), 7.76 (d, *J*=16 Hz, 1H, Olefinic-H), 7.59 (d, *J*=8.5 Hz, 2H, Ar-H), 7.53 (d, *J*=16 Hz, 1H, Olefinic-H), 7.40 (d, *J*=8.5 Hz, 2H, Ar-H), 6.99 (d, *J*=8.5 Hz, 2H, Ar-H), 4.06 (t, *J*=6.5 Hz, 2H, -OCH_2-),1.86-1.81 (m, 2H, -OCH_2CH_2-), 1.52-1.30 (m,

14H, -C<u>H</u>$_2$-), 0.90 (t, *J*=6.5 Hz, 3H, -C<u>H</u>$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 188.3, 163.2, 142.3, 136.1, 133.6, 130.8, 130.6, 130.4, 129.4, 129.1, 128.6, 127.1, 122.3, 114.3, 77.3, 77.0, 76.7, 68.3, 31.9, 29.7, 29.6, 29.5, 29.3, 29.1, 26.0, 22.7, 14.1. MS (m/z): 400.2 $(M+H)^+$. Anal. Calcd. For. $C_{25}H_{31}ClO_2$: C. 75.26; H. 7.83; Found: C. 75.52; H. 7.76.

3-(4-Chlorophenyl)-1-(4-(dodecyloxy)phenyl)prop-2-en-1-one (3e). Yield: 0.92 g (78 %), m.p. 116-117 °C. FTIR (cm^{-1}): 2913, 2848, 1657, 1597, 1252, 1170, 1013, 815. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.04 (d, *J*=9 Hz, 2H, Ar-<u>H</u>), 7.76 (d, *J*=15.5 Hz, 1H, Olefinic-<u>H</u>), 7.59 (d, *J*=8.5 Hz, 2H, Ar-<u>H</u>), 7.53 (d, *J*=15.5 Hz, 1H, Olefinic-<u>H</u>), 7.41 (d, *J*=9 Hz, 2H, Ar-<u>H</u>), 6.99 (d, *J*=8.5 Hz, 2H, Ar-<u>H</u>), 4.06 (t, J=6.5 Hz, 2H, -OC<u>H</u>$_2$-), 1.85-1.82 (m, 2H, -OCH$_2$C<u>H</u>$_2$-), 1.52-1.29 (m, 18H, -C<u>H</u>$_2$-), 0.90 (t, *J*=6.5 Hz, 3H, -C<u>H</u>$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 188.4, 163.2, 142.3, 136.2, 133.6, 130.8, 130.7, 130.5, 129.5, 129.2, 128.7, 127.2, 122.4, 114.4, 77.4, 77.0, 76.7, 68.3, 31.9, 29.7, 29.6, 29.4, 29.1, 26.0, 22.7, 14.1. MS (m/z): 428.2 $(M+H)^+$. Anal. Calcd. For. $C_{27}H_{35}ClO_2$: C. 75.94; H. 8.26; Found: C. 75.69; H. 8.34.

3-(4-Chlorophenyl)-1-(4-(tetradecyloxy)phenyl)prop-2-en-1-one (3f). Yield: 1.56 g (72 %), m.p. 119-120 °C. FTIR (cm^{-1}): 2912, 2846, 1654, 1597, 1251, 1170, 1014, 814. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.04 (d, *J*=9 Hz, 2H, Ar-<u>H</u>), 7.76 (d, *J*= 16 Hz, 1H, Olefinic-<u>H</u>), 7.59 (d, *J*=9 Hz, 2H, Ar-<u>H</u>), 7.53 (d, *J*=16 Hz, 1H, Olefinic-<u>H</u>), 7.41 (d, *J*=8.5 Hz, 2H, Ar-<u>H</u>), 6.99 (d, *J*=8.5 Hz, 2H, Ar-<u>H</u>), 4.06 (t, *J*=6.5 Hz, 2H, -OC<u>H</u>$_2$-),1.86-1.81 (m, 2H, -OCH$_2$C<u>H</u>$_2$-), 1.51-1.28 (m, 22H, -C<u>H</u>$_2$-), 0.90 (t, *J*=6.5 Hz, 3H, -C<u>H</u>$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 188.4, 165.1, 163.1, 162.6, 142.5, 131.4, 131.3, 130.8, 130.7, 130.2, 130.1, 121.6, 116.1, 115.9, 114.3, 68.3, 31.9, 29.5, 29.3, 29.1, 26.0, 22.6, 14.1. MS (m/z): 456.2 $(M+H)^+$. Anal. Calcd. For. $C_{29}H_{39}ClO_2$: C. 76.54; H. 8.64; Found: C. 76.82; H. 8.71.

3-(4-Bromophenyl)-1-(4-(decyloxy)phenyl)prop-2-en-1-one (3g). Yield: 1.2 g (77 %), m.p. 149-150 °C. FTIR (cm^{-1}): 2917, 2852, 1658, 1594, 1249, 1165, 1014, 814. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.01 (d, *J*=8 Hz, 2H, Ar-<u>H</u>), 7.66 (d, *J*=16 Hz, 1H, Olefinic-<u>H</u>), 7.54 (d, *J*=8 Hz, 2H, Ar-<u>H</u>), 7.47 (d, *J*=8.5 Hz, 2H, Ar-<u>H</u>), 7.04 (d, *J*=16 Hz, 1H, Olefinic-<u>H</u>), 6.96 (d, *J*=8.5 Hz, 2H, Ar-<u>H</u>), 4.03 (t, *J*=6.6 Hz, 2H, -OC<u>H</u>$_2$-),1.85-1.78 (m, 2H, -OCH$_2$C<u>H</u>$_2$-), 1.49-1.25 (m, 14H, -C<u>H</u>$_2$-), 0.88 (t, *J*=6.6 Hz, 3H, -C<u>H</u>$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 188.3, 163.2, 142.4, 134.1, 132.1, 131.6, 130.8, 130.6, 130.5, 129.7, 127.5, 124.5, 122.4, 114.4, 77.3, 77.0, 76.7, 68.3,

31.9, 29.7, 29.6, 29.4, 29.3, 29.1, 26.0, 22.7, 14.1. MS (m/z): 444.1 $(M+H)^+$. Anal. Calcd. For. $C_{25}H_{31}BrO_2$: C. 67.72; H. 7.05; Found: C. 67.97; H. 7.13.

3-(4-Bromophenyl)-1-(4-(dodecyloxy)phenyl)prop-2-en-1-one (3h). Yield: 1.4 g (68 %), m.p. 115-116 °C. FTIR (cm^{-1}): 2911, 2857, 1658, 1598, 1249, 1165, 1014, 814. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.02 (d, *J*=8.5 Hz, 2H, Ar-H), 7.65 (d, *J*=16 Hz, 1H, Olefinic-H), 7.54 (d, *J*=8.5 Hz, 2H, Ar-H), 7.49 (d, *J*=8.5 Hz, 2H, Ar-H), 7.04 (d, *J*=16 Hz, 1H, Olefinic-H), 6.96 (d, *J*=8.5 Hz, 2H, Ar-H), 4.03 (t, *J*=6.6 Hz, 2H, -OCH_2-),1.84-1.77 (m, 2H, -OCH$_2$CH_2-), 1.51-1.27 (m, 18H, -CH_2-), 0.88 (t, *J*=6.6 Hz, 3H, -CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 188.3, 163.2, 142.4, 134.0, 132.1, 131.6, 130.8, 130.6, 130.5, 129.7, 127.5, 124.5, 122.4, 114.3, 68.3, 31.9, 29.6, 29.5, 29.3, 29.1, 26.0, 22.7, 14.1. MS (m/z): 472.1 $(M+H)^+$. Anal. Calcd. For. $C_{27}H_{35}BrO_2$: C. 68.78; H. 7.48; Found: C. 68.94; H. 7.41.

3-(4-Bromophenyl)-1-(4-(tetradecyloxy)phenyl)prop-2-en-1-one (3i). Yield: 1.1 g (75 %), m.p. 119-120 °C. FTIR (cm^{-1}): 2918, 2855, 1650, 1596, 1244, 1162, 1011, 814. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.00 (d, *J*=8.8 Hz, 2H, Ar-H), 7.72 (d, *J*=15.6 Hz, 1H, Olefinic-H), 7.54 (d, *J*=8.8 Hz, 2H, Ar-H), 7.49 (d, *J*=8 Hz, 2H, Ar-H), 7.04 (d, *J*=15.6 Hz, 1H, Olefinic-H), 6.96 (d, *J*=8.8 Hz, 2H, Ar-H), 4.03 (t, *J*=6.6 Hz, 2H, -OCH_2-),1.83-1.77 (m, 2H, -OCH$_2$CH_2-), 1.50-1.26 (m, 22H, -CH_2-), 0.87 (t, *J*=6.8 Hz, 3H, -CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 188.3, 163.2, 142.4, 134.0, 132.1, 131.6, 130.8, 130.6, 130.5, 129.7, 127.5, 124.5, 122.4, 114.3, 68.3, 31.9, 29.6, 29.5, 29.3, 29.1, 26.0, 22.7, 14.1. MS (m/z): 500.2 $(M+H)^+$. Anal. Calcd. For. $C_{29}H_{39}BrO_2$: C. 69.73; H. 7.87; Found: C. 69.49; H. 7.82.

1-(4-(Decyloxy)phenyl)-3-(4-nitrophenyl)prop-2-en-1-one (3j). Yield: 1.2 g (78 %), m.p. 109-110 °C. FTIR (cm^{-1}): 2918, 2850, 1654, 1597, 1255, 1172, 1022, 822. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.29 (d, *J*=9 Hz, 2H, Ar-H), 8.05 (d, *J*=9 Hz, 2H, Ar-H), 7.81 (d, *J*=15 Hz, 1H, Olefinic-H), 7.79 (d, *J*=8.5 Hz, 2H, Ar-H), 7.67 (d, *J*=15 Hz, 1H, Olefinic-H), 7.00 (d, *J*=8.5 Hz, 2H, Ar-H), 4.06 (t, *J*=6.5 Hz, 2H, -OCH_2-),1.87-1.81 (m, 2H, -OCH$_2$CH_2-), 1.52-1.30 (m, 14H, -CH_2-), 0.90 (t, *J*=7 Hz, 3H, -CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 187.6, 163.5, 163.1, 148.3, 141.3, 140.5, 130.9, 130.5, 130.3, 130.1, 130.0, 128.7, 126.5, 125.6, 124.1, 114.4, 114.2, 114.0, 77.3, 77.0, 76.6, 68.3, 68.2, 31.8, 29.6, 29.5, 29.3, 29.0, 26.2, 25.9, 22.6, 14.1. MS (m/z):

410.2 $(M+H)^+$. Anal. Calcd. For. $C_{25}H_{31}NO_4$: C. 73.32; H. 7.63; N. 3.42; Found: C. 73.64; H. 7.59; N. 3.49.

1-(4-(Dodecyloxy)phenyl)-3-(4-nitrophenyl)prop-2-en-1-one (3k). Yield: 1.45 g (76 %), m.p. 114-115 °C. FTIR (cm^{-1}): 2916, 2849, 1657, 1598, 1256, 1173, 1012, 812. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.28 (d, *J*=9 Hz, 2H, Ar-H), 8.05 (d, *J*=9 Hz, 2H, Ar-H), 7.81 (d, *J*=15 Hz, 1H, Olefinic-H), 7.79 (d, *J*=9 Hz, 2H, Ar-H), 7.66 (d, *J*=15 Hz, 1H, Olefinic-H), 7.00 (d, *J*=9 Hz, 2H, Ar-H), 4.06 (t, *J*=6.5 Hz, 2H, -OCH_2-),1.85-1.82 (m, 2H, -OCH_2CH_2-), 1.50-1.28 (m, 18H, -CH_2-), 0.89 (t, *J*=6.7 Hz, 3H, -CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 187.7, 163.5, 163.1, 148.4, 141.3, 140.5, 130.9, 130.5, 130.3, 130.2, 130.0, 128.8, 126.5, 125.6, 124.1, 114.5, 114.2, 114.1, 77.3, 77.0, 76.7, 68.4, 68.2, 43.9, 31.9, 29.6, 29.5, 29.3, 29.1, 26.3, 25.9, 22.7, 14.1. MS (m/z): 438.2 $(M+H)^+$. Anal. Calcd. For. $C_{27}H_{35}NO_4$: C. 74.11; H. 8.06; N. 3.20; Found: C. 74.37; H. 8.12; N. 3.26.

3-(4-Nitrophenyl)-1-(4-(tetradecyloxy)phenyl)prop-2-en-1-one (3l). Yield: 0.88 g (77 %), m.p. 119-120 °C. FTIR (cm^{-1}): 2915, 2848, 1654, 1597, 1256, 1170, 1014, 814. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.29 (d, *J*=9 Hz, 2H, Ar-H), 8.05 (d, *J*=9 Hz, 2H, Ar-H), 7.81 (d, *J*= 15 Hz, 1H, Olefinic-H), 7.79 (d, *J*=8.5 Hz, 2H, Ar-H), 7.66 (d, *J*=15 Hz, 1H, Olefinic-H), 7.00 (d, *J*=9 Hz, 2H, Ar-H), 4.06 (t, *J*=6.5 Hz, 2H, -OCH_2-),1.85-1.82 (m, 2H, -OCH_2CH_2-), 1.50-1.28 (m, 22H, -CH_2-), 0.89 (t, *J*=7 Hz, 3H, -CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 187.72, 163.5, 163.1, 148.4, 141.3, 140.5, 131.0, 130.5, 130.3, 130.2, 130.1, 128.8, 128.5, 126.5, 125.7, 124.2, 123.7, 114.5, 114.2, 114.1, 68.4, 31.9, 29.6, 29.5, 29.3, 29.1, 26.3, 25.9, 22.7, 14.1. MS (m/z): 466.3 $(M+H)^+$. Anal. Calcd. For. $C_{29}H_{39}NO_4$: C. 74.81; H. 8.44; N. 3.01; Found: C. 74.57; H. 8.39; N. 3.08.

3-(Pyridin-4-yl)-1-(4-(tetradecyloxy)phenyl)prop-2-en-1-one (3m). Yield: 0.8 g (66 %), m.p. 79-80 °C. FTIR (cm^{-1}): 2917, 2846, 1652, 1599, 1254, 1167, 1012, 814. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.67 (d, *J*=6 Hz, 2H, Pyridine-H), 8.01 (d, *J*=8.8 Hz, 2H, Ar-H), 7.67 (s, 1H, Olefinic-H), 7.46 (d, *J*=6 Hz, 2H, Pyridine-H), 7.26 (s, 1H, Olefinic-H), 6.98 (d, *J*=8.8 Hz, 2H, Ar-H), 4.04 (t, *J*=6.6 Hz, 2H, -OCH_2-), 1.85-1.78 (m, 2H, -OCH_2CH_2-), 1.50-1.26 (m, 22H, -CH_2-), 0.87 (t, *J*=6.8 Hz, -CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 187.9, 165.5, 150.6, 142.3, 140.6, 131.0, 130.5, 130.3, 130.2, 126.0, 122.0, 114.5, 68.4, 31.9, 29.6, 29.5, 29.3, 29.1,

25.9, 22.7, 14.1. MS (m/z): 422.3 $(M+H)^+$. Anal. Calcd. For. $C_{28}H_{39}NO_2$: C. 79.76; H. 9.32; N. 3.32; Found: C. 79.99; H. 9.25; N. 3.39.

3-(4-(Decyloxy)phenyl)-1-(thiophen-2-yl)prop-2-en-1-one (3n). Yield: 1.1 g (71 %), m.p. 102-103 °C. FTIR (cm^{-1}): 2917, 2846, 1653, 1599, 1254, 1167, 1013, 814. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.88 (d, *J*=15 Hz, 1H, Olefinic-H), 7.71 (d, *J*=3.2 Hz, 1H, Ar-H (Thiophene)), 7.60 (d, *J*=11 Hz, 2H, Ar-H), 7.54 (d, *J*=15 Hz, 1H, Olefinic-H), 7.49 (d, *J*=4.4 Hz, 1H, Ar-H (Thiophene)), 7.14 (t, *J*=4.4 Hz, 1H, Ar-H (Thiophene)), 7.02 (d, *J*=8.8 Hz, 2H, Ar-H), 4.01 (t, *J*= 6.4 Hz, 2H, -OCH_2-), 1.83-1.79 (m, 2H, -OCH_2CH_2-), 1.49-1.28 (m, 14H, -CH_2-), 0.88 (t, *J*=6.8 Hz, 3H, -CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 182.1, 161.4, 145.8, 144.0, 133.4, 131.4, 130.3, 129.1, 127.2, 119.1, 114.9, 114.7, 68.2, 31.9, 29.3, 29.1, 26.0, 22.7, 14.1. MS (m/z): 371.2 $(M+H)^+$. Anal. Calcd. For. $C_{23}H_{30}O_2S$: C. 74.55; H. 8.16; S. 8.65; Found: C. 74.83; H. 8.10; S. 8.58.

General procedure for synthesis of target methoxypyridine derivatives (4a-n)

Compound **3a-n** (1 equivalent) was added slowly to a freshly prepared solution of sodium methoxide (10 equivalent of sodium in methanol) while stirring. Malononitrile (1.2 equivalent) was then added with continuous stirring at room temperature until the precipitate separates out. The solid separated was collected by filtration, washed with methanol and recrystallized from ethanol.

6-(4-(Decyloxy)phenyl)-4-(4-fluorophenyl)-2-methoxynicotinonitrile (4a). Yield: 1.4 g (68 %). FTIR (cm^{-1}): 2914, 2851, 2218, 1588, 1231, 1170, 1016, 825. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.06 (d, *J*=8.4 Hz, 2H, Ar-H), 7.66-7.62 (m, 2H, Ar-H), 7.37 (s, 1H, Pyridine-H), 7.26-7.20 (m, 2H, Ar-H), 6.99 (d, *J*=8.4 Hz, 2H, Ar-H), 4.19 (s, 3H, -OMe of Pyridine), 4.02 (t, *J*=6 Hz, 2H, -OCH_2-), 1.83-1.80 (m, 2H, -OCH_2CH_2-), 1.65-1.27 (m, 14H, -CH_2-), 0.87 (t, *J*=6.6 Hz, 3H, -CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.0, 162.4, 161.4, 157.9, 155.3, 132.5, 130.4, 129.4, 128.8, 116.1, 114.8, 112.3, 91.8, 68.2, 54.5, 31.8, 29.5, 29.3, 29.1, 26.0, 22.6, 14.0. MS (m/z): 461.2 $(M+H)^+$. Anal. Calcd. For. $C_{29}H_{33}FN_2O_2$: C. 75.62; H. 7.22; N. 6.08; Found: C. 75.91; H. 7.17; N. 6.16.

6-(4-(Dodecyloxy)phenyl)-4-(4-fluorophenyl)-2-methoxynicotinonitrile (4b). Yield: 1.2 g (73 %). FTIR (cm^{-1}): 2917, 2855, 2218, 1592, 1240, 1174, 1016, 827. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.06 (d, *J*=8.8 Hz, 2H, Ar-H), 7.66-7.62 (m, 2H, Ar-H), 7.37 (s, 1H, Pyridine-H),7.26-7.20 (m, 2H, Ar-H), 6.99 (d, *J*=8.8 Hz, 2H, Ar-H), 4.19 (s, 3H, -OMe of Pyridine), 4.02 (t, *J*=6.6 Hz, 2H, -OCH_2-), 1.83-1.80 (m, 2H, -OCH_2-CH_2-), 1.64-1.26 (m, 18H, -OCH_2-), 0.87 (t, *J*=6.6 Hz, -CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.0, 162.4, 161.3, 157.9, 155.2, 132.5, 130.4, 129.4, 128.8, 116.1, 114.7, 112.3, 91.8, 68.2, 54.5, 31.9, 29.6, 29.5, 29.3, 29.1, 26.0, 22.6, 14.0. MS (m/z): 489.3 $(M+H)^+$. Anal. Calcd. For. $C_{31}H_{37}FN_2O_2$: C. 76.20; H. 7.63; N. 5.73; Found: C. 76.45; H. 7.59; N. 5.77.

4-(4-Fluorophenyl)-2-methoxy-6-(4-(tetradecyloxy)phenyl)nicotinonitrile (4c). Yield: 1.45 g (78 %). FTIR (cm^{-1}): 2913, 2850, 2216, 1589, 1235, 1172, 1012, 825. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.06 (d, *J*=8.8 Hz, 2H, Ar-H), 7.66-7.62 (m, 2H, Ar-H), 7.37 (s, 1H, Pyridine-H), 7.26-7.22 (m, 2H, Ar-H), 6.99 (d, *J*=8.8 Hz, Ar-H), 4.19 (s, 3H, -OMe of Pyridine), 4.02 (t, *J*=6.6 Hz, 2H, -OCH_2-), 1.83-1.79 (m, 2H, -OCH_2CH_2-), 1.69-1.25 (m, 22H, -CH_2-), 0.87 (t, *J*=6.6 Hz, -CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.0, 162.4, 161.4, 157.9, 155.3, 132.5, 130.4, 129.4, 128.8, 116.1, 114.8, 112.3, 91.8, 68.2, 54.5, 31.9, 29.6, 29.5, 29.3, 29.1, 26.0, 22.6, 14.0. MS (m/z): 517.3 $(M+H)^+$. Anal. Calcd. For. $C_{33}H_{41}FN_2O_2$: C. 76.71; H. 8.00; N. 5.42; Found: C. 76.42; H. 8.06; N. 5.47.

4-(4-Chlorophenyl)-6-(4-(decyloxy)phenyl)-2-methoxynicotinonitrile (4d). Yield: 1.22 g (68 %). FTIR (cm^{-1}): 2911, 2849, 2216, 1583, 1237, 1173, 1020, 823. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.07 (d, *J*=9 Hz, 2H, Ar-H), 7.60 (d, *J*=8.5 Hz, 2H, Ar-H), 7.52 (d, *J*=9 Hz, 2H, Ar-H), 7.38 (s, 1H, Pyridine-H), 7.01 (d, *J*=9 Hz, 2H, Ar-H), 4.21 (s, 3H, -OMe of Pyridine), 4.09-4.04 (m, 2H, -OCH_2-), 1.86-1.81 (m, 2H, -OCH_2CH_2-), 1.52-1.27 (m, 14H, -CH_2-), 0.90 (t, *J*=7 Hz, 3H, -CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.0, 161.4, 158.0, 155.1, 136.2, 134.9, 129.7, 128.8, 115.6, 114.8, 112.2, 91.8, 68.1, 54.5, 31.9, 29.7, 29.5, 29.4, 29.3, 26.0, 22.6, 14.1. MS (m/z): 477.2 $(M+H)^+$. Anal. Calcd. For. $C_{29}H_{33}ClN_2O_2$: C. 73.02; H. 6.97; N. 5.87; Found: C. 73.28; H. 6.93; N. 5.81.

4-(4-Chlorophenyl)-6-(4-(dodecyloxy)phenyl)-2-methoxynicotinonitrile (4e). Yield: 1.15 g (71 %). FTIR (cm^{-1}): 2914, 2851, 2215, 1589, 1238, 1172, 1014, 824. ^{1}H NMR (500 MHz,

$CDCl_3$) δ (ppm) 8.07 (d, *J*=9 Hz, 2H, Ar-H), 7.60 (d, *J*=8.5 Hz, 2H, Ar-H), 7.52 (d, *J*=8.5 Hz, 2H, Ar-H), 7.38 (s, 1H, Pyridine-H), 7.01 (d, *J*=9 Hz, 2H, Ar-H), 4.21 (s, 3H, -OMe of Pyridine), 4.07-4.04 (m, 2H, -OCH_2-), 1.85-1.81 (m, 2H, -OCH_2CH_2-), 1.51-1.29 (m, 18H, -CH_2-), 0.90 (t, *J*=7 Hz, 3H, -CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.0, 161.4, 158.0, 155.1, 136.2, 134.9, 129.7, 128.8, 115.6, 114.8, 112.2, 91.8, 68.1, 54.5, 31.9, 29.7, 29.5, 29.4, 29.3, 26.0, 22.6, 14.1. MS (m/z): 505.2 $(M+H)^+$. Anal. Calcd. For. $C_{31}H_{37}ClN_2O_2$: C. 73.72; H. 7.38; N. 5.55; Found: C. 73.97; H. 7.44; N. 5.49.

4-(4-Chlorophenyl)-2-methoxy-6-(4-(tetradecyloxy)phenyl)nicotinonitrile (4f). Yield: 1.4 g (75 %). FTIR (cm^{-1}): 2919, 2850, 2224, 1588, 1242, 1175, 1016, 828. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.07 (d, *J*=9 Hz, 2H, Ar-H), 7.60 (d, *J*=8.5 Hz, 2H, Ar-H), 7.52 (d, *J*=8.5 Hz, 2H, Ar-H), 7.38 (s, 1H, Pyridine-H), 7.01 (d, *J*=9 Hz, Ar-H), 4.21 (s, 3H, -OMe of Pyridine), 4.06-4.04 (m, 2H, -OCH_2-), 1.86-1.81 (m, 2H, -OCH_2CH_2-), 1.52-1.28 (m, 22H, -CH_2-), 0.89 (t, *J*=7 Hz, -CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 164.9, 161.4, 157.9, 155.3, 132.5, 130.4, 129.4, 128.8, 116.2, 114.8, 112.3, 91.9, 68.2, 54.5, 31.9, 29.6, 29.5, 29.3, 29.1, 26.0, 22.6, 14.1. MS (m/z): 533.3 $(M+H)^+$. Anal. Calcd. For. $C_{33}H_{41}ClN_2O_2$: C. 74.34; H. 7.75; N. 5.25; Found: C. 74.59; H. 7.80; N. 5.17.

4-(4-Bromophenyl)-2-(4-(decyloxy)phenyl)-6-methoxypyridine (4g). Yield: 1.25 g (79 %). FTIR (cm^{-1}): 2918, 2854, 1587, 1238, 1171, 1020, 827. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.03 (d, *J*=14.4 Hz, 2H, Ar-H), 7.59 (d, *J*=10.8 Hz, Ar-H), 7.51 (d, *J*=10.8 Hz, 2H, Ar-H), 7.43 (s, 1H, Pyridine-H), 6.98 (d, *J*=14.4 Hz, 2H, Ar-H), 6.78 (s, 1H, Pyridine-H), 4.07 (s, 3H, -OMe of Pyridine), 4.02 (t, *J*=6.6 Hz, 2H, -OCH_2-), 1.85-1.78 (m, 2H, -OCH_2CH_2-), 1.55-1.26 (m, 14 H, -CH_2-), 0.89 (t, *J*=7.5 Hz, 3H, -CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 164.4, 160.1, 155.2, 150.6, 137.9, 132.1, 131.4, 128.8, 128.0, 123.1, 114.5, 110.5, 105.8, 68.1, 53.3, 32.7, 30.0, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.9, 27.4, 26.0, 22.6, 19.7, 14.1. MS (m/z): 497.2 $(M+H)^+$. Anal. Calcd. For. $C_{28}H_{34}BrNO_2$: C. 67.74; H. 6.90; N. 2.82; Found: C. 67.48; H. 6.99; N. 2.85.

4-(4-Bromophenyl)-2-(4-(dodecyloxy)phenyl)-6-methoxypyridine (4h). Yield: 1.4 g (82 %). FTIR (cm^{-1}): 2920, 2855, 1591, 1235, 1171, 1020, 827. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.04 (d, *J*=14.4 Hz, 2H, Ar-H), 7.58 (d, *J*=10.8 Hz, Ar-H), 7.53 (d, *J*= 10.8 Hz, 2H, Ar-H), 7.43 (s, 1H, Pyridine-H), 6.98 (d, *J*= 14.4 Hz, 2H, Ar-H), 6.77 (s, 1H, Pyridine-H), 4.06 (s, 3H, -OMe

of Pyridine), 4.02 (t, *J*=6.6 Hz, 2H, -OC<u>H</u>$_2$-), 1.85-1.78 (m, 2H, -OCH$_2$C<u>H</u>$_2$-), 1.55-1.26 (m, 18 H, -C<u>H</u>$_2$-), 0.89 (t, *J*=7.5 Hz, 3H, -C<u>H</u>$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.0, 161.4, 158.0, 155.0, 135.4, 132.2, 129.9, 128.8, 128.0, 124.5, 114.8, 110.5, 105.8, 68.2, 53.4, 31.9, 29.6, 29.5, 29.3, 29.2, 29.1, 26.0, 22.6, 14.1. MS (m/z): 523.2 $(M+H)^+$. Anal. Calcd. For. $C_{30}H_{38}BrNO_2$: C. 68.69; H. 7.30; N. 2.67; Found: C. 68.92; H. 7.39; N. 2.63.

4-(4-Bromophenyl)-2-methoxy-6-(4-(tetradecyloxy)phenyl)pyridine (4i). Yield: 1.28 g (71 %). FTIR (cm^{-1}): 2917, 2849, 1594, 1231, 1168, 1020, 827. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.03 (d, *J*=12.4 Hz, 2H, Ar-<u>H</u>), 7.65 (d, *J*=12.8 Hz, Ar-<u>H</u>), 7.50 (d, *J*=12.8 Hz, 2H, Ar-<u>H</u>), 7.43 (s, 1H, Pyridine-<u>H</u>), 6.98 (d, *J*=12.4 Hz, 2H, Ar-<u>H</u>), 6.78 (s, 1H, Pyridine-<u>H</u>), 4.06 (s, 3H, -OMe of Pyridine), 4.02 (t, *J*=6.6 Hz, 2H, -OC<u>H</u>$_2$-), 1.84-1.77 (m, 2H, -OCH$_2$C<u>H</u>$_2$-), 1.53-1.26 (m, 22 H, -C<u>H</u>$_2$-), 0.89 (t, *J*=7.5 Hz, 3H, -C<u>H</u>$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 164.4, 160.1, 155.2, 150.6, 137.8, 132.1, 131.3, 128.8, 128.0, 123.1, 114.5, 110.5, 105.8, 68.1, 53.3, 31.5, 29.6, 29.5, 29.4, 29.3, 29.2, 28.9, 27.4, 26.0, 22.6, 19.7, 14.1. MS (m/z): 553.5 $(M+H)^+$. Anal. Calcd. For. $C_{32}H_{42}BrNO_2$: C. 69.55; H. 7.66; N. 2.53; Found: C. 69.76; H. 7.62; N. 2.48.

2-(4-(Decyloxy)phenyl)-6-methoxy-4-(4-nitrophenyl)pyridine (4j). Yield: 0.94 g (46 %). FTIR (cm^{-1}): 2915, 2853, 1579, 1241, 1173, 1020, 829. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.41 (d, *J*=9 Hz, 2H, Ar-<u>H</u>), 8.08 (d, *J*=9 Hz, 2H, Ar-<u>H</u>), 7.83 (d, *J*=8.5 Hz, 2H, Ar-<u>H</u>), 7.60 (s, 1H, Pyridine-<u>H</u>), 7.10 (s, 1H, Pyridine-<u>H</u>), 7.02 (d, *J*=8.5 Hz, 2H, Ar-<u>H</u>), 4.20 (s, 3H, OMe of Pyridine),4.07-4.04 (m, 2H, -OC<u>H</u>$_2$-), 1.85-1.82 (m,2H, -OCH$_2$C<u>H</u>$_2$-), 1.51-1.28 (m, 14H, -C<u>H</u>$_2$-), 0.90 (t, *J*=7 Hz, 3H, -C<u>H</u>$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 164.9, 161.7, 158.5, 148.6, 142.6, 129.5, 128.9, 124.1, 115.1, 114.9, 112.0, 68.2, 54.7, 31.9, 29.6, 29.5, 29.3, 29.1, 26.0, 22.6, 14.1. MS (m/z): 463.3 $(M+H)^+$. Anal. Calcd. For. $C_{28}H_{34}N_2O_4$: C. 72.70; H. 7.41; N. 6.06; Found: C. 72.46; H. 7.47; N. 6.09.

2-(4-(Dodecyloxy)phenyl)-6-methoxy-4-(4-nitrophenyl)pyridine (4k). Yield: 0.8 g (48 %). FTIR (cm^{-1}): 2913, 2850, 1576, 1238, 1171, 1018, 827. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.40 (d, *J*=8.5 Hz, 2H, Ar-<u>H</u>), 8.08 (d, *J*=8.5 Hz, 2H, Ar-<u>H</u>), 7.82 (d, *J*=8.5 Hz, 2H, Ar-<u>H</u>), 7.60 (s, 1H, Pyridine-<u>H</u>), 7.10 (s, 1H, Pyridine-<u>H</u>), 7.02 (d, *J*=8.5 Hz, 2H, Ar-<u>H</u>), 4.23 (s, 3H, -OMe of Pyridine), 4.05 (t, *J*=6.5 Hz, 2H, -OC<u>H</u>$_2$-), 1.87-1.81 (m, 2H, -OCH$_2$C<u>H</u>$_2$-), 1.52-1.27 (m, 18H, -C<u>H</u>$_2$-), 0.90 (t, *J*=7 Hz, 3H, -C<u>H</u>$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 164.9, 161.7,

158.5, 148.6, 142.6, 129.5, 128.9, 124.1, 115.1, 114.9, 112.0, 68.2, 54.7, 31.9, 29.6, 29.5, 29.3, 29.1, 26.0, 22.6, 14.1. MS (m/z): 491.3 $(M+H)^+$. Anal. Calcd. For. $C_{30}H_{38}N_2O_4$: C. 73.44; H. 7.81; N. 5.71; Found: C. 73.71; H. 7.76; N. 5.66.

2-Methoxy-4-(4-nitrophenyl)-6-(4-(tetradecyloxy)phenyl)pyridine (4l). Yield: 0.7 g (55 %). FTIR (cm^{-1}): 2914, 2850, 1586, 1250, 1173, 1022, 828. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.40 (d, *J*=9 Hz, 2H, Ar-H), 8.08 (d, *J*=9 Hz, 2H, Ar-H), 7.82 (d, *J*=8.5 Hz, 2H, Ar-H), 7.71 (s, 1H, Pyridine-H),7.30 (s, 1H, Pyridine-H), 7.02 (d, *J*=8.5 Hz, 2H, Ar-H), 4.23 (s, 3H, -OMe of Pyridine), 4.06 (t, *J*=6.5 Hz, 2H, -OCH$_2$-), 1.85-1.82 (m, 2H, -OCH$_2$CH$_2$-), 1.51-1.28 (m, 22H, -CH$_2$-), 0.89 (t, *J*=7 Hz, 3H, -CH$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 164.9, 161.7, 158.5, 148.6, 142.6, 129.5, 128.9, 124.1, 115.1, 114.9, 112.0, 68.2, 54.7, 31.9, 29.6, 29.5, 29.3, 29.1, 26.0, 22.6, 14.1. MS (m/z): 519.3 $(M+H)^+$. Anal. Calcd. For. $C_{32}H_{42}N_2O_4$: C. 74.10; H. 8.16; N. 5.40; Found: C. 74.41; H. 8.12; N. 5.46.

2-Methoxy-4-(pyridin-4-yl)-6-(4-(tetradecyloxy)phenyl)pyridine (4m). Yield: 0.88 g (68 %). FTIR (cm^{-1}): 2918, 2851, 1588, 1254, 1176, 1022, 828. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.72 (d, *J*=6 Hz, 2H, Pyridine-H), 8.03 (d, *J*=8.8 Hz, 2H, Ar-H), 7.54 (d, *J*=6 Hz, 2H, Pyridine-H), 7.48 (s, 1H, Pyridine-H), 6.99 (d, *J*=8.8 Hz, 2H, Ar-H), 6.84 (s, 1H, Pyridine-H), 4.08 (s, 3H, -OMe of Pyridine), 4.02 (t, *J*=6.6 Hz, 2H, -OCH$_2$-), 1.85-1.78 (m, 2H, -OCH$_2$CH$_2$-), 1.51-1.26 (m, 22H, -CH$_2$-), 0.87 (t, *J*=6.8 Hz, 3H, -CH$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 164.5, 160.3, 155.6, 150.5, 149.1, 146.3, 131.1, 129.8, 128.9, 128.1, 122.6, 121.5, 114.9, 114.6, 110.2, 106.1, 68.1, 53.5, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 26.0, 22.6, 14.1. MS (m/z): 475.4 $(M+H)^+$. Anal. Calcd. For. $C_{31}H_{42}N_2O_2$: C. 78.44; H. 8.92; N. 5.90; Found: C. 78.68; H. 8.97; N. 5.83.

4-(4-(Decyloxy)phenyl)-2-methoxy-6-(thiophen-2-yl)nicotinonitrile (4n). Yield: 1.2 g (79 %). FTIR (cm^{-1}): 2917, 2850, 2213, 1580, 1514, 1450, 1365, 1236, 1135, 1031, 828, 692. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.71 (d, *J*=3.2 Hz, 1H, Thiophene-H), 7.60 (d, *J*=8.8 Hz, 2H, Ar-H), 7.49 (d, *J*=4.8 Hz, 1H, Thiophene-H), 7.32 (s, 1H, Pyridine-H), 7.14 (t, *J*=4.8 Hz, 1H, Thiophene-H), 7.02 (d, *J*=8.8 Hz, 2H, Ar-H), 4.15 (s, 3H, -OMe of Pyridine), 4.02 (t, *J*= 6.4 Hz, 2H, -OCH$_2$-), 1.83-1.79 (m, 2H, -OCH$_2$CH$_2$-), 1.49-1.28 (m, 14H, -CH$_2$-), 0.88 (t, *J*=6.8 Hz, 3H, -CH$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.0, 160.7, 156.2, 152.8, 143.4, 129.7, 129.6, 128.0, 126.8, 115.9, 114.9, 111.5, 110.4, 91.9, 68.2, 54.6, 31.8, 29.5, 29.3, 29.1, 26.0, 22.6, 14.0.

MS (m/z): 449.2 $(M+H)^+$. Anal. Calcd. For. $C_{27}H_{32}N_2O_2S$: C. 72.29; H. 7.19; N. 6.24; S. 7.15; Found: C. 72.55; H. 7.24; N. 6.27; S. 7.10.

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Supporting Information

Copies of ^1H and ^{13}C NMR spectra of target compounds. The bond lengths (Å) and bond angles (°) for compounds **4m** and **4n**. Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Center with the deposition numbers 978127 and 978451. Copy of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk].

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