Study of the mesomorphic behaviour through the structure modification of azo and acetylene pyridinium and imidazolium-based ionic liquid crystals

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ABSTRACT
In this work, 14 pyridinium and imidazolium-based ionic liquid crystal (ILC) with azo (N=N) and acetylene (C≡C) as linking group were synthesised in high yields and completely characterised. The structure of the molecules were planned in order to allow a complete investigation on how modifications such as presence and position of charges, linking group, number of alkoxy chains and their length affect the thermal stability and liquid crystalline behaviour. All compounds were thoroughly investigated using polarised optical microscopy (POM), differential scanning calorimetry (DSC), X-ray diffraction (XRD) measurements and thermogravimetric analysis (TGA). While the presence of charges favoured a liquid crystalline behaviour, especially SmA (and SmA\(_2\)) phase, a decrease of thermal stability was noticed. A strong dependence of the charge position and a preference for monolayer or bilayer molecular organisation was observed. On the other hand, it was demonstrated that the addition of a second alkoxy chain promoted layer distortions in some molecules, resulting in the formation of Sm\(_{\text{à}}\) and Cub phases. Also a direct comparison between the N=N and C≡C linking groups was realised, along with further comparison with literature data. The structure–properties are investigated in detail.

1. Introduction
The research and interest in ionic liquid crystals (ILCs) have been increasing in the last years, due to their intrinsic combination of ionic liquid and liquid crystal properties [1]. These kind of materials possess a good chemical and thermal stability, low vapour pressure, high conductivity and a wide electrochemical window, as well as self-assembly behaviour [2,3]. A great advantage showed by ILC is their tunable conductivity in function of their mesomorphic properties [4], so that the conduction can be in one, two or three dimension [5–7]. Owing to these characteristics, ILCs are finding application in different knowledge areas, such as ionic conductivity [8,9], sensors [10,11], water treatment [12], organic light-emitting diodes and other optoelectronic devices [13], dye-sensitised solar cells (DSSC) [14,15] among other functional materials [16].

Imidazole and pyridine are some of the most employed fundamental units aiming cationic ILC [17,18]. Materials based on these heterocycles can be
classified into three typical classes: (1) the heterocycle can be part of the rigid core with one or two final alky chains. These molecules usually show smectogenic behaviour of the mono- and bilayer type [5,19]; (2) the organic cation is separated from the rigid core by an alky chain spacer and the mesogen can be constitute by one or two alky chains [20,21]; (3) the ILC has three or more lateral alky chains [22,23].

In order to obtain best materials with more efficient applications, it is necessary to understand the relationship between the molecular structure and the properties of the ILC. Currently, many different studies have been made aiming a better comprehension of this structure–properties relation, where different factors were investigated such as length [20] and number of alky chains [22], linking group [23], number [24] and position of the organic ion on the rigid core, size of alky chain spacer [20] and counterion type [20,25]. Nevertheless, each minimal structural change can have a strong effect on the materials properties, improving simultaneously some characteristics but worsening others. For this reason it is of vital importance to keep improving the deep understanding of the structure–properties relationship, allowing a continuous search of new and better materials.

In this context, this study presents a systematic investigation of the structure–properties relationship of azo and acetylenes pyridinium and \( N \)-methylimidazolium ILCs. For this, 15 molecules (ionic and nonionic) comprising different structural modifications such as presence of charges, linking group, number and length of alkoxy chains were investigated. Their properties were compared with each other and also with similar molecules published in the literature, being the effect of every structural parameter discussed and correlated. We believe that this work complements the knowledge of ionic liquid crystalline compounds.

### 2. Results and discussion

In order to gain a better understanding of the structure–property relationship and continue the work published by Westphal et al. [17], several new ionic calamitic liquid crystals were planned and synthesised. All products are comprised of a linear structure with an azo (\(N=N\)) or \(C=C\) bond as a central linking group. The structure of all molecules can be seen in the schematic illustration in Figure 1.

The variety of molecules prepared in this study was planned so as to allow a systematic study of the structure–property relationship. As observed in Figure 1, compound \( \text{XY-10Br} \) is comprised of a linear structure, with a charge placed at the end of the rigid core and two long aliphatic chains, one on each side. On the other hand, compound \( \text{XY-1I} \) has a short aliphatic chain on the pyridinium side, allowing the determination of the influence of the chain length. Compounds \( \text{XY-Dec} \) and \( \text{XY-Met} \) are both very similar to \( \text{XY-10Br} \) and \( \text{XY-1I} \), but without the presence of explicit charges, enabling an in-depth understanding of the influence of the charges. Molecule \( \text{XY-8Im} \) (also ionic) was planned to have a charge at the end of the aliphatic chain, separated from the rigid core by an \(8C\) aliphatic chain. The number of aliphatic chains can also be investigated from the molecules planned in this work. Besides, the change in the connecting group from \(N=N\) to \(C=C\), but without modifying the linearity of the structure, enhances our understanding of the influence of the linking group. In addition, due to the similarity between this structure and molecules published in previous paper, the influence of the linear \(N=N\) and \(C=C\) connecting groups could also be compared with that of the 1,3,4-oxadiazole heterocycle [17], which promotes the bend of the molecule and provides a strong lateral dipole moment [26–28].

#### 2.1. Synthesis

The procedures used in the synthesis of the calamitic ILCs described in this work, and the respective non-
charged molecules, are outlined in Schemes 1–3. Despite the similarity between the structures (see Figure 1), the approach to obtaining the products differed due to the need for different starting reagents. Detailed descriptions of the experimental procedure and characterisation can be found in the experimental section below. It is important to note that the compound CC-Dec has been previously described in the literature in two different publications [29,30] and therefore it was not synthesised in this study.

The synthesis of the first group of molecules is described in Scheme 1. The pyridinium ionic molecules were obtained following a linear synthetic route. The 4-aminopyridine (I) was first diazotised and then coupled with phenol, resulting in an azo N=N bond. Alkylation of the hydroxyl group through a Williamson etherification using K$_2$CO$_3$ resulted in the long chain intermediate 2. Reaction of the pyridine group with bromodecane or iodomethane, using acetonitrile as the solvent, resulted in the two pyridinium ionic compounds NN-10Br and NN-1I, respectively. The ionic imidazolium product and the nonionic compounds were obtained through another synthetic pathway. The synthesis began with the alkylation of the 4-hydroxyacetanilide (3), followed by hydrolysis of the amide group, resulting in the long chain aniline intermediate (4). Diazotisation of aniline 4 and coupling with phenol in basic aqueous media, resulted in the phenol derivative 5, which was alkylated with bromodecane or iodomethane, resulting in both nonionic molecules (NN-Dec and NN-Met). For the imidazolium product, the phenol 5 was alkylated with excess (3 equivalents) of 1,8-dibromooctane, ensuring exclusively mono-alkylation (6). In the last step, the reaction of 6 with 1-methylimidazole using microwave resulted in the product NN-8Im.

The synthesis of the second group of compounds (Scheme 2), which contain an additional alkoxy group, is similar to the synthetic route employed for the first group. It started with the mono-alkylation of catechol (7) to produce the intermediate 8, which was coupled with the freshly prepared diazonium salt of 4-aminopyridine (1). It is important to note that, when catechol (7) or 1,2-alkoxybenzene was used in the coupling step, the desired azo compound was not obtained. Therefore, we opted to use the mono-alkylated catechol (8), adapting a procedure described in the literature [31]. Although this methodology gave the desired molecule (9), the yield was very low (13%) even after several modifications of the experimental procedure (base, solvent and temperature). Nevertheless, the amount of product obtained was sufficient to continue with the synthetic route. In the next step, the remaining hydroxyl group was submitted to a new alkylation reaction, resulting in the pyridine derivative containing two long alkoxy chains (10). The pyridine intermediate 10 was later reacted with bromodecane and iodomethane, resulting in both pyridinium ionic compounds in high yields (CaNN-10Br and CaNN-11I, respectively).

Scheme 1. Synthesis of the final azo calamitic liquid crystals. Reagents: (i) HBF$_4$ (48%), NaNO$_2$; (ii) phenol, NaOH, H$_2$O; (iii) n-C$_{10}$H$_2$I, Br, K$_2$CO$_3$, butanone; (iv) n-C$_{10}$H$_2$I, Br, acetonitrile; (v) CH$_3$I, acetonitrile; (vi) HCl, H$_2$O; (vii) HBF$_4$ (48%), NaNO$_2$, THF, H$_2$O; (viii) CH$_3$I, K$_2$CO$_3$, acetone; (ix) BrC$_6$H$_4$I, Br, K$_2$CO$_3$, butanone; (x) 1-methylimidazole, microwave.
Scheme 2. Synthetic route for the catechol-derived final compounds. Reagents: (i) \( n-C_{10}H_{21}Br, K_2CO_3, DMF \); (ii) HBF\(_4\) (48%), NaNO\(_2\); (iii) TEA, THF; (iv) \( n-C_{10}H_{21}Br, K_2CO_3, TBAB \) (for catechol), butanone; (v) \( n-C_{10}H_{21}Br, \) acetone; (vi) \( CH_3I, \) acetone; (vii) NaNO\(_2\), HNO\(_3\), CH\(_3\)Cl\(_2\); (viii) \( H_2, Pd/C \) (10%), THF, MeOH; (ix) HBF\(_4\) (48%), \( t\)-butyl nitrite, THF, CH\(_2\)Cl\(_2\); (x) phenol, NaOH, THF, H\(_2\)O; (xi) \( CH_3I, K_2CO_3, \) acetone; (xii) Br\(C_6H_{15}Br, K_2CO_3, \) butanone; (xiii) 1-methylimidazole.

Scheme 3. Synthesis of the final target compounds containing the C≡C bond as a central connecting unit. Reagents: (i) \( n-C_{10}H_{21}Br, K_2CO_3, \) butanone; (ii) 2-methyl-3-butyn-2-ol, PdCl\(_2\)(PPh\(_3\))\(_2\), PPh\(_3\), Cul, dry TEA; (iii) NaOH, toluene; (iv) HBF\(_4\) (48%), NaNO\(_2\); (v) KI, acetone, H\(_2\)O; (vi) PdCl\(_2\)(PPh\(_3\))\(_2\), PPh\(_3\), Cul, dry TEA, dry THF; (vii) \( n-C_{10}H_{21}Br, \) acetone; (viii) \( CH_3I, \) acetone; (ix) PdCl\(_2\)(PPh\(_3\))\(_2\), PPh\(_3\), Cul, dry TEA; (x) KOH, THF, MeOH, H\(_2\)O; (xi) Br\(C_6H_{15}Br, K_2CO_3, \) butanone; (xii) 1-methylimidazole, microwave.
The other molecules of this group were obtained from the same starting reagent. Catechol was initially alkylated, followed by nitration of the aromatic ring and reduction of the nitro group through a catalytic hydrogenation, resulting in the aniline. Diazotisation of the aniline using t-butyl nitrite and coupling with phenol in basic medium resulted in the phenol. Alkylation of the phenol group of with bromodecane or iodomethane resulted in the nonionic molecules (CaNN-Dec and CaNN-Met), while the use of excess of 1,8-dibromooctane led to the intermediate. The imidazolium ionic compound (CaNN-8Im) was obtained by the reaction of the alkyl bromide with 1-methylimidazole.

The last class of compounds synthesised in this work, containing a C≡C bond instead of an azo (N=N) bond, was prepared according to Scheme 3. The synthesis of the pyridinium derivatives started with the alkylation of 4-bromophenol, followed by a Sonogashira cross-coupling with 2-methyl-3-butyln-3-ol and deprotection of the alkynol, resulting in the terminal alkyne. In parallel, 4-iodopyridine was prepared by a Sandmeyer reaction between the diazonium salt of the 4-aminopyridine and KI. Both the terminal alkyne and 4-iodopyridine were coupled together by a Sonogashira cross-coupling reaction employing PdCl\(_2\)(PPh\(_3\))\(_3\) as the catalyst. The pyridine group of the resulting pyridine derivative was alkylated with a decyl or a methyl group, resulting in the ionic products CC-10Br and CC-11, respectively.

The terminal alkyne is also a key intermediate in the synthesis of the other target molecules of the third class. A Sonogashira cross-coupling reaction between the alkyne and 1-iodo-4-methoxybenzene resulted in the nonionic tolane CC-Met. For the imidazolium derivative, an attempt to reach compound through a direct cross-coupling reaction between the alkyne and 1-(8-bromoctyloxy)-4-iodobenzene was unsuccessful due to a partial exchange of the terminal bromine for iodine during the reaction. Therefore, the intermediate had to be discarded, since it would result in an impure counterion (Br\(^-\) and I\(^-\)).

The structure and purity of all compounds synthesised in this work were confirmed by techniques such as melting point (m.p.) and \(^1\)H and \(^13\)C nuclear magnetic resonance (NMR). In addition, all final compounds were characterised by high-resolution mass spectroscopy (HR-MS). All techniques confirmed the alkylation of the pyridine and imidazole groups, generating the ionic molecules. By NMR, the presence of additional peaks around 5 ppm (\(^1\)H) and 50–60 ppm (\(^13\)C) attributed to the H and C near the quaternised amine, allied to the chemical shift of the peaks referent to the pyridine moiety confirm the alkylation. HR-MS shows the presence of the additional chain for the cation, while the anion was also detected. But the irrefutable confirmation comes from the single-crystal structure obtained for compound CC-11 (Figure 2), where the molecular structure of the ionic compound shows the covalent bond between the methyl and pyridine groups, together with the counterion (I\(^-\)) and two water molecules (Crystallographic data can be found in the Supplemental Online Material).

2.2. Thermal investigations

The thermal properties of the calamitic compounds (ionic and nonionic) were fully investigated through polarised optical microscopy (POM), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) techniques. Further information on the molecular organisation in the liquid crystalline phases was obtained by X-ray diffraction (XRD) measurements at the mesophase temperature. The phase...
transition temperatures (and respective enthalpies) and the mesophase and decomposition temperatures of the target compounds are summarised in Table 1. Due to the fact that many compounds decompose before reaching the liquid state, all temperatures and enthalpies in Table 1 relate to the first heating scan. The discussion on the thermal and liquid crystalline behaviour is organised into topics, allowing a better understanding of the structure–property relationships of ILCs.

### 2.2.1. Thermal stability

The thermal stability of the products synthesised in this work was determined by TGA under an inert atmosphere (N₂). Since liquid crystals and their properties are very sensitive to impurities and given that ILCs usually have lower thermal stability [17,22,32], we consider the very beginning of mass loss to indicate the decomposition temperature (see Table 1). It can be noted that many molecules synthesised in this work start to decompose before reaching the isotropisation temperature. However, this behaviour is not uncommon for ILCs [1,2]. Many other compounds, notably methyl pyridinium compounds (see Table 1), start to decompose a few degrees above the temperature at which they become fluid, that is, after melting.

On carrying out a comparison within the same class of compounds (NN, CaNN or CC), the noncharged molecules show higher thermal stability compared with the ionic molecules (these being stable for an additional 30–50°C). An exception is the compound CaNN-Met, which starts to decompose at 154°C, around the same temperature as the respective pyridinium iononic molecules (CaNN-10Br and CaNN-11).

However, the mass loss rate at this temperature is slow, and less than 2% of the mass is lost up to 250°C. Among the ILCs, the decomposition starts at higher temperatures for the imidazolium derivatives (XY-8Im), these being, on average, stable for an additional 50°C compared with the respective pyridinium compounds. This higher thermal stability of imidazolium compounds has already been described in other publications [17,33].

In terms of the thermal stability, no significant change was observed for the azo compounds when an additional alkoxy chain is present in the molecular structure. However, the same is not true when the linking unit is changed from N=N (NN molecules) to C=C (CC molecules). In this case, the triple bonded compounds start to decompose at slightly higher temperatures. This is more evident for the ionic compounds where the positive charge is conjugated to the linking group, that is, for the pyridinium derivatives. For the nonionic molecules or when the charge is isolated from the linking groups by an insulating alkyl chain (i.e., the imidazolium molecules), this effect is not as significant. An even greater thermal stability is observed when both N=N and C=C linking groups are replaced by the 1,3,4-oxadiazole heterocyclic, as can be noted when comparing with the molecules previously published by Westphal et al. (Table 5) [17].

The pyridinium oxadiazole compound similar to the XY-10Br molecules is around 10°C more stable than CC-10Br and more stable (by 40°C) than the azo derivatives. The oxadiazole similar to XY-11 also has a higher stability. Despite the fact that the imidazolium group is separated from the linking units by a long insulating alkyl chain and that no significant difference

| Compound | Transitions[a–d] – T(ΔH)[c] | T_{dec} [°C] |
|----------|-------------------------------|---------|
| NN-10Br  | Cr – 119 [11.4] – SmA – 138 [3.5] – Iso | 153 |
| NN-11    | Cr – 121 [42.3] – SmA₂ – dec | 139 |
| NN-8Im   | Cr – 113 [22.6] – SmC₂ – 162 [0.8] – SmA₂ – dec | 201 |
| NN-Dec   | Cr – 102 [46.3] – SmC – 106 [1.0] – N – 108 [2.1] – Iso | 240 |
| NN-Met   | Cr – 101 [44.5] – Iso | 237 |
| CaNN-10Br | Cr – 86 [21.9] – SmA – 119 [1.2] – Iso | 154 |
| CaNN-11  | Cr – 154 [7.7] – MesX – dec | 161 |
| CaNN-8Im | Cr – 105 [59.8] – Col(SmA₂) – 125 [0.4] – SmA₂ – 164 [3] – Cub – dec | 204 |
| CaNN-Dec | Cr – 76 [56.0] – Iso | 253 |
| CaNN-Met | Cr – 75 [24.6] – Cr’ – 81 [26.8] – Iso | 154 |
| CC-10Br  | Cr – 174 [10.1] – SmA – dec | 183 |
| CC-11    | Cr – 121 [6.2] – Cr – 133 [11.9] – SmA₂ – dec | 165 |
| CC-8Im   | Cr – 99 [6.1] – Cr – 111 [18.1] – SmC₂ – 146 [0.9] – SmA₂ – dec | 207 |
| CC-Dec   | Cr – 86 [52.3] – SmC – 89 [2.9] – SmA – 95 [3.6] – N – 101 [3.3] – Iso | – |
| CC-Met   | Cr – 87 [53.2] – Iso | 242 |

[a]Cr and Cr’: crystal phases; SmA: smectic A phase; SmC: smectic C phase; N: nematic phase; MesX: unknown phase; Col: columnar phase; SmA₂: modulated smectic A phase; Cub: cubic phase; Iso: isotropic liquid; dec: decomposition; subscript 2 (, ) indicates a bilayer organisation; 
[c]Transitions determined by DSC (peak temperatures) during the first heating scan using a heating/cooling rate of 10°C min⁻¹; 
[d]Temperatures are given in °C and enthalpy values in kJ mol⁻¹. 
[c] Determined by TGA measurements under nitrogen atmosphere with a heating rate of 10°C min⁻¹. The values refer to the very beginning of decomposition; 
[f] Not observed from DSC measurements; 
[g] Phase transition temperatures and enthalpies provided in the literature [29].
in the decomposition temperatures is observed between the XY-8Im molecules in this work, it was surprising that the presence of the 1,3,4-oxadiazole heterocycle as a linking group increased the thermal stability of the ionic compound by more than 40°C.

For the 1,3,4-oxadiazole pyridinium ILCs described by Westphal et al. [17], and many other ILCs reported in the literature [16], the thermal mass loss curve can be divided into different regions, the first being related to the loss of the alkyl group together with its counter-ion, as in a reverse Menschutkin reaction [34]. The same behaviour was observed for compounds CaNN-1I and CC-1I. However, based on the thermal mass loss pattern, this cannot be verified for NN-1I or for the pyridinium XY-10Br molecules. Also, the imidazolium class of compounds containing N=N or C≡C linking groups do not follow this behaviour, as previously demonstrated for oxadiazole derivatives [17]. For the nonionic molecules, the thermal mass loss occurs mainly in one step, following the same behaviour observed for similar oxadiazole molecules.

2.2.2. Investigation on liquid crystalline properties

After a complete structural characterisation and determination of the thermal stability, the liquid crystalline properties were investigated. The compounds were firstly investigated by POM, where thermal phase transitions were determined and the mesophases initially characterised through their optical textures [35]. Later, DSC measurements confirmed the phase transitions and gave the enthalpy values related to the transitions. Finally, the XRD analysis of some compounds confirmed the molecular organisation in the liquid crystalline state [36]. In this section, the liquid crystalline behaviour of every compound synthesised in this work will be fully described. In subsequent sections, the structure–property relationships for the ILCs will be outlined.

Compound NN-10Br, containing two long aliphatic chains and in which the charge is located in the centre of the molecular structure, at the end of the rigid core (Figure 1), shows two thermal transitions. At 119°C, it melts to a liquid crystalline phase and at 138°C a transition to the isotropic liquid (Iso) state is observed, resulting in a low-stability mesophase (19°C). Based on the POM, the mesophase was identified as a SmA phase, since the texture showed oily streaks (Figure 3(a)) on heating, which is commonly observed for ILCs [2]. Large areas with an isotropic-like texture indicate that an average homeotropic alignment is favoured. On cooling from the isotropic state, a fan-shaped texture (Figure 3(b)) [35] was observed, which is consistent with the observations on heating.

As summarised in Table 2, the layered molecular arrangement of the SmA phase was confirmed by the XRD measurements (Figure 4). The diffraction pattern shows a typical smectic organisation with several peaks in the small-angle region, which follow a reciprocal spacing ratio of 1:2:3... (d_10, d_20, d_30, ... respectively). The diffuse peak with maxima around 0.45 nm is related to the average lateral distance between the molecules in the liquid crystalline state and it indicates the fluidity of the phase. A comparison between the first diffraction peak (d_10), which is related to the layer spacing, and the molecular length at the most stretched conformation (L) resulted in a d_10/L value of 0.82. The smaller layer spacing, when compared to the molecular length (d_10/L < 1), indicates that the molecules are arranged in a monolayered SmA phase with an antiparallel organisation of the mesogens. Also, this
suggests an intermolecular interdigitation of the long aliphatic chains, as schematised in Figure 5(a).

Compound NN-1I, which is similar to NN-10Br but contains a short chain on the pyridinium side, melts at 121°C to a SmA phase and mass loss starts at around 139°C, before it reaches the Iso. On cooling from the SmA phase, no crystallisation is observed even at room temperature, the compound remaining in a supercooled state. Crystallisation is only observed when the sample is heated again, occurring at around 60°C. This supercooled state was confirmed by DSC (Figure 6(a)) and XRD measurements. In the POM analysis only an oily streak texture was observed on heating. Due to the impossibility of reaching the Iso and promote a better organisation of the material in the mesophase, XRD analysis was performed during the heating process. The diffraction pattern ratifies the SmA observations by POM, with the presence of the d_{10} and d_{30} peaks (see Table 2), with a d_{20}/d_{10} ratio of ≈2. The measured layer spacing (d_{10}) was 3.84 nm while the calculated molecular length (L) was only 2.54 nm, resulting in a d_{10}/L value of 1.51. The layer spacing of the SmA phase is larger than the size of one NN-1I molecule, but significantly smaller than twice the molecular length. This suggests a bilayered structure (SmA_2) where the polar pyridinium groups of adjacent layers are organised in an antiparallel mode, as schematised in Figure 5(b). Also, the d_{10}/L value indicates complete alkyl chain interdigitation. In principle, a monolayer SmA phase with molecules in an antiparallel order (Figure 5(a)) could also be expected, resulting in an estimated layer thickness of 3.88 nm. However, since the molecules contain only one long aliphatic chain and are aligned in an antiparallel mode, significant interdigitation of the alkyl chain is expected. This would reduce the layer spacing to around 2.9 nm and therefore this type of organisation can be discarded.

Compound NN-8Im contains an imidazolium unit at the end of one of the aliphatic chains. It melts at 113°C to a SmC phase and at 162°C a transition to a SmA phase can be observed, which remains until around 200°C when the decomposition process starts. On heating, the texture of the SmC phase could not be clearly observed in the POM analysis, inhibiting accurate attribution. For the SmA phase, the formation of an oily streak texture with large areas of homeotropic alignment (Figure 3(c)) indicate an on average orthogonal mesophase, as previously discussed for the other compounds. The higher the temperature the larger the homeotropic areas. On cooling from the SmA phase, a schlieren–marble-like texture (Figure 3(d)) can be observed for the SmC phase. On further cooling, the birefringence increases until 103°C, when the crystallisation takes place.

XRD measurements confirmed a lamellar structure for both the SmA and SmC phases. As described for NN-1I, the compound NN-8Im also shows a bilayered organisation in the smectic phases. Similar behaviour for the end chain imidazolium unit with small chains has been

| Compound | mesophase (T/°C) | d/nm (d_{hk}) | L/nm a | d_{10}/L |
|----------|------------------|--------------|--------|----------|
| NN-10Br  | SmA (130)        | 3.01 (d_{10})| 3.67   | 0.82     |
|          |                  | 1.52 (d_{20})|        |          |
|          |                  | 1.01 (d_{30})|        |          |
|          |                  | 0.76 (d_{40})|        |          |
|          |                  | 0.45 (diff)  |        |          |
| NN-1I    | SmA_2 (140)      | 3.15 (d_{10})| 2.54   | 1.51     |
|          |                  | 1.93 (d_{20})|        |          |
|          |                  | 0.45 (diff)  |        |          |
| NN-8Im   | SmA_2 (200)      | 6.29 (d_{10})| 3.95   | 1.59     |
|          |                  | 2.09 (d_{20})|        |          |
|          |                  | 0.46 (diff)  |        |          |
|          | SmC_2 (140)      | 5.89 (d_{10})|        |          |
|          |                  | 2.95 (d_{20})|        |          |
|          |                  | 1.96 (d_{30})|        |          |
|          |                  | 0.45 (diff)  |        |          |

aMolecular length was estimated using the ChemBio3D Ultra software (version 11.0.1) and assuming the molecule to be in the most stretched conformation;
bDiffraction peak not entirely visible and estimated from the d_{30} and d_{10} diffraction peaks as an average value.
described by Laschat et al. [37]. Owing to the large molecular length and, consequently, bilayer thickness, the first diffraction peak could not be completely observed, being mostly cut off. However, the second and third diffraction peaks have a ratio of 1.5, strongly indicating that they are indeed peaks $d_{20}$ and $d_{30}$, respectively. Therefore, the layer thickness ($d_{10}$) could be estimated, resulting in a value of 6.29 nm at 200°C (Table 2). The $d_{10}/L$ value of 1.59 calculated for the NN-8Im SmA phase suggests a bilayered organisation (SmA$_2$) with strong interdigitation of the alkyl chains, as schematised in Figure 5(c). A bilayer structure with complete interdigitation of the terminal chains and maintaining the most stretched conformation would result in a layer thickness of 6.73 nm, that is, larger than the estimated layer of 6.29 nm. This could be due to the fact that the alkyl chains are not in the most stretched conformation or may suggest some interpenetration of the imidazolium group. However, in the latter case, we would expect a splitting of the wide-angle diffuse peaks indicating that the average lateral packing between the alkyl chains and that between the imidazolium groups differ. However, this is not clearly observed from the XRD measurements.

The XRD data for compound NN-8Im in the SmC phase still indicate a bilayered organisation, where the bilayer is now tilted with respect to the layer normal. Based on the layer shrinkage from the SmA$_2$ to the SmC$_2$ phase and using the cosine relation, we roughly estimate a tilt angle of around 20°.

An ionic azobenzene compound, similar to NN-8Im, but with slightly shorter aliphatic chain (C8) and a guanidinium group instead of an imidazolium ionic was described by Wuckert et al. [38]. The guanidinium derivative melts to a bilayered SmA phase at 100°C and the clearing point is observed at 132°C. A direct comparison between the guanidinium and imidazolium derivatives

![Figure 5](image-url)

**Figure 5.** Schematic illustration showing three different molecular organisations suggested for the SmA phase of the ionic liquid crystal: (a) monolayer SmA phase; (b) bilayer SmA phase (SmA$_2$); (c) bilayer SmA phase (SmA$_2$) for the imidazolium compounds, in which the charge is located at the end of the molecular structure.

![Figure 6](image-url)

**Figure 6.** DSC for compounds NN-1I (a) and CaNN-8Im (b).
shows significant higher mesophase stability for later (NN-8Im), with 88°C against 32°C. Interestingly, the presence of the ionic group at the end of the aliphatic chain promoted a bilayered smectic phase for both compounds. However, while for the guanidinium molecule only a SmA phase was described, a SmC phase was also observed for the NN-8Im ionic molecule. Wuckert et al. also demonstrated that segregation between the ionic head group and the nonionic part of the molecule is more important to the layer formation than the parallel orientation of the molecule, showing the importance of the Coulombic interactions.

The nonionic molecule NN-Dec shows a very narrow liquid crystalline range, melting at 102°C to a SmC phase, changing to a nematic (N) phase at 106°C and reaching the Iso at 108°C. Mesophases were attributed mainly based on the textures observed by POM, since no accurate XRD measurements could be obtained due to the narrow liquid crystalline range. On cooling from the Iso, at the Iso - N phase transition typical nematic droplets were observed, which coalesced into a schlieren, marble or thread-like texture, depending on the plate region and sample thickness (Figure 3(e)). On further cooling, the texture changed to a focal conic and broken fan shape with the extinction brushes inclined in relation to the polarisers (Figure 3(f)), suggesting an SmC phase. At 95°C crystallisation is observed. In contrast, the shorter nonionic molecule NN-Met did not show any liquid crystalline behaviour, melting directly to the Iso at 101°C.

The liquid crystalline properties of the azo compounds with an additional alkoxy chain (CaNN) were also thoroughly investigated. The phase transitions are summarised in Table 1 while the XRD crystallographic data are detailed in Table 3. Similarly to the results described for NN-10Br, compound CaNN-10Br also shows an enantiotropic SmA phase with decomposition starting several degrees above the isotropisation point. On heating, the Cr – SmA phase transition is observed at 86°C while the SmA – Iso phase transition occurs at 119°C, resulting in a mesophase range of 33°C on heating. As previously described for other compounds, the POM analysis revealed an oily streak texture in an antiparallel form (subject to alkyl chain interdigitiation) are responsible for the molecular organisation. Due to the limited temperature range available for the XRD measurements allied to the low decomposition temperature and high sample viscosity, it was difficult to obtain a suitable XRD pattern. The diffractogram shows one low intensity small-angle diffraction peak (3.76 nm) in addition to the diffuse peak (0.45 nm). A comparison of the small-angle diffraction peak value with the calculated molecular length results in a d10/L ratio of 1.47, which is larger than the size of one molecule but significantly smaller than two molecules. This suggests that the diffraction peak indeed corresponds to the d10 and that two molecules aligned in an antiparallel form (subject to alkyl chain interdigitation) are responsible for the molecular organisation. The great difference between the volume fraction of the aromatic (and ionic) section and the alkoxy chains, allied to the fact that an antiparallel

### Table 3. Crystallographic data for the CaNN group of liquid crystalline compounds, calculated molecular length (L) and d10/L ratio.

| Compound | Mesophase (T/°C) | d/nm (hkl) | L/nm a | d10/L | Notes |
|----------|------------------|------------|--------|-------|-------|
| CaNN-10Br | SmA (100) | 2.92 (10) | 3.68 | 0.79 | Molecular length was estimated using the ChemBio3D Ultra software (version 11.0.1) and assuming the molecule to be in the most stretched conformation; |
| | SmA (160) | 3.76 (10) | 2.55 | 1.47 |
| CaNN-10Br | SmA (150) | 5.84 (10) | 3.98 | 1.49 | Diffraction peak not entirely visible and estimated from the d_30 and d_90 diffraction peaks as an average value. |
| CaNN-10Br | SmA (130) | 6.09 (10) | 3.98 | 1.53 |

a: Molecular length was estimated using the ChemBio3D Ultra software (version 11.0.1) and assuming the molecule to be in the most stretched conformation;
alignment is occurring (head-to-head), could promote an disruption of the layers into ribbons. This would result in a modulated SmA phase ($\text{SmA}_2$) or even in hexagonal columnar phase ($\text{Col}_h$), agreeing with the columnar kind texture observed by POM \[39-41\]. However, unfortunately no reliable mesophase attribution can be made with the results collected and therefore, the mesophase is simply referred to as MesX (see Table 1).

For the imidazolium compound, CaNN-8Im, an interesting polymorphism was noted. On heating, the molecule initially melts to a columnar phase at 105°C, followed by a transition to a SmA phase at 125°C. In the POM, no clear texture was observed for the lower phase on heating, while oily streaks texture with large homeotropic regions was present in the SmA phase (Figure 7(c)). The homeotropic regions increased in size when the sample was further heated or maintained for a few minutes at the same temperature. At around 164°C, a phase transition was observed by POM, while no peak appeared in the DSC measurements (Figure 6(b)). The isotropic-like texture of the homeotropically aligned sample changed and isotropic crystal-like domains grew in a slow and continuous way (Figure 7(d)), as typically observed for cubic phases, until the whole sample was modified. The phase transition was more easily detected by slightly decrossing the polarisers. No other textural changes were observed until the decomposition temperature was reached, and the texture also remained unchanged during the cooling process. No SmA phase was observed in the POM, with the cubic phase remaining in a supercooled state until the transition to the lower phase around 125°C. The transition occurred slowly and pseudo-focal conic texture was observed, suggesting a columnar phase (Figure 7(e,f)). At around 95°C the sample crystallised.

XRD measurements were performed for compound CaNN-8Im (Table 3) during the heating process for all the mesophases. For the columnar phase, the measurements were also done on the cooling process from the cubic phase, with similar results. A lamellar structure for the SmA was confirmed by the presence of $d_{10}$, $d_{20}$ and $d_{30}$ diffraction peaks. Similarly to what was described for compound NN-8Im, the first diffraction peak ($d_{10}$) was actually not completely observed, being partially cut off. However, the second and third diffraction peaks have a ratio of 1.5, strongly indicating that they are indeed peaks $d_{30}$ and $d_{30}$, respectively. Therefore, the layer thickness ($d_{10}$) could be estimated, resulting in a value of 5.84 nm at 150°C. As also discussed for NN-8Im, the $d_{10}$/L value of 1.49 suggests a bilayered organisation ($\text{SmA}_2$) with strong interdigitation of the alkyl chain. For the cubic phase, only one portion of the small angle diffraction could be observed, hindering any interpretation. Therefore, the cubic attribution was made by textures observed by POM. For the lower temperature mesophase, initially described by POM as columnar, surprisingly a lamellar organisation was suggested by the XRD pattern. The $d_{10}$/L ratio for this phase is similar to the one observed for the SmA$_2$ phase, indicating the same bilayered organisation. We believe that the pseudo-focal conic texture observed by POM could arise from a modulation of the SmA$_2$ layer, where the layers are broken ribbons which are shifted along the layer normal by $\frac{1}{2}$, thus becoming organised on a centred rectangular lattice ($\text{SmA}_2$) \[39,40\]. The layer thickness ($d_{10}$) in this phase is slightly larger than the one determined for the higher
temperature SmA$_2$ phase. This can be attributed to an increase of the molecular lateral packing with the decrease of the temperature, leading to an additional chain stretching. The SmA$_2$, SmA$_2$, Cub phase sequence during the heating process can be understood by the different volume fraction occupied by each region of the molecular structure. At lower temperatures, it is likely that the volume fraction of the alkyl chains is larger than that of the ionic group. Therefore, a disruption of the ionic layers into ribbons could happen, resulting in the SmA$_2$ organisation. By increasing the temperature, the polar parts become more mobile and occupy a larger volume, promoting the fusion of the broken layers and resulting in the SmA$_2$ phase. With further heating, the alkyl chains expansion becomes dominant, leading to a curvature of the layer and resulting in the cubic phase.

The two nonionic molecules containing additional alkoxy chains did not show any liquid crystalline behaviour, melting directly to the Iso, as described in Table 1.

The CC class of compound, which contains an acetylene linking group instead of an azo linkage, shows similar mesomorphic behaviour in comparison with the NN class. The CC-10Br and CC-1I molecules melt to a SmA phase and start losing mass before the Iso state is reached, resulting in a narrow mesophase range in both cases. By POM, oily streaks textures were mainly observed for the SmA phase. For a thick sample of compound CC-10Br near the decomposition temperatures, regions of focal conic fan-shaped texture were also observed (Figure 8(a)). Compound CC-1I shows a second crystalline phase (Cr’), whose texture is not really characteristic of crystalline compounds (Figure 8(b)). However, when analysing this phase by POM, no fluidity can be noticed for the material sandwiched between the glass plates. Besides, some diffraction peaks can be observed at higher angles at XRD measurements. Therefore, we strongly believe that this is not a liquid crystalline phase, being described as a Cr phase. XRD measurements for both compounds during the heating process confirmed the SmA organisation (Table 4). However, as already described for the NN compounds in this study, the calculated d$_{10}$/L value (< 1) for compound CC-10Br suggests a monolayered phase (Figure 5(a)), while a d$_{10}$/L of 1.42 for CC-1I indicates a bilayered organisation (Figure 5(b)). Single-crystal structure of the crystalline phase of compound CC-1I (see Supplemental Online Material) shows this

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**Figure 8.** (Colour online) Textures observed for the CC liquid crystalline compounds: (a) CC-10Br at 182°C on the heating process; (b) CC-1I at 143°C on the cooling process; (c) oily streaks textures for the SmA phase of CC-8Im at 150°C during the heating process; (d) CC-8Im at 135°C on cooling from the SmA phase.
Table 4. Crystallographic data for the CC group of liquid crystalline compounds, calculated molecular length (L) and \( d_{10}/L \) ratio.

| Compound | mesophase (T/°C) | d/nm (hk) | L/nm \( ^a \) | \( d_{10}/L \) |
|----------|------------------|-----------|----------------|----------------|
| CC-10Br  | SmA (180)        | 3.08 (10) | 3.72           | 0.83           |
|          |                  | 1.55 (20) |                |                |
|          |                  | 0.46 (diff) |            |                |
| CC-11    | SmA (160)        | 3.61 (10) | 2.55           | 1.42           |
|          |                  | 0.45 (diff) |            |                |
| CC-8Im   | SmA (180)        | 6.40 (10) \(^b\) | 3.97 | 1.61 |
|          |                  | 3.18 (20) |                |                |
|          |                  | 2.15 (30) |                |                |
|          |                  | 0.45 (diff) |            |                |
| SmC\(_2\) (140) | 5.80 (10) \(^b\) |            |            |                |

\( ^a \)Molecular length was estimated using the ChemBio3D Ultra software (version 11.0.1) and assuming the molecule to be in the most stretched conformation.

\( ^b \)Diffraction peak not entirely visible and estimated from the \( d_{20} \) and \( d_{30} \) diffraction peaks as an average value.

Table 5. Transition temperatures, associated enthalpy values and thermal stability of the 1,3,4-oxadiazole compounds \[17\]. Reproduced by permission of The Royal Society of Chemistry.

| Compound | Transitions – \( T(\Delta H) \) | \( T_{dec} \) |
|----------|----------------------------------|-------------|
| 1–8Im-Br | Cr – 181.9 [21.2] – SmA           | 193         |
| 1–11     | Cr – dec                         | 192         |
| 1–8Im-Br | Cr – 144.2 [58.9] – SmA – 225.7 [1.8] – Iso | 251         |
| 1–10     | Cr – 129.5 [71.1] – Iso           | 284         |
| 1–1      | Cr – 99.7 [31.7] – Iso            | 258         |
| 2–10Br   | Cr – 148.1 [11.3] – SmA           | 194         |
| 2–11     | Cr – dec                         | 185         |
| 2–8Im-Br | Cr – 67.3 [48.7] – MesX – 118.9 [0.4] – SmA\(_2\) – 227.1 [0.3] – Iso | 245         |
| 2–10     | Cr – 77.4 [73.3] – Iso            | 283         |
| 2–1      | Cr – 82.0 [57.3] – Iso            | 261         |

antiparallel arrangement of the molecules, with a head-to-head approximation of the pyridinium groups, in agreement with the molecular organisation schematically illustrated by Figure 5(b) and the observations made by XRD for the SmA\(_2\) phase.

The CC-8Im compound melts at 111°C to smectic C phase, changing to smectic A phase at 146°C. The transition to the Iso phase was not observed since thermal decomposition starts at 207°C. When analysing a sample of CC-8Im by POM during the heating process, a marble and an oily streaks texture are observed for the SmC and SmA phase (Figure 8(c)), respectively. Whereas on cooling, a schlieren texture was observed for the SmC phase (Figure 8(d)). XRD measurements confirm the lamellar structure for both SmA and SmC phases (Table 4). Following the same behaviour as already described for NN-8Im and CaNN-8Im, due to the large layer thickness the first diffraction peak (\( d_{10} \)) could not be completely observed due to small angles limitations of the XRD equipment. Therefore, the \( d_{10} \) peak was estimated using the \( d_{20} \) and \( d_{30} \) peaks, resulting in a layer thickness of 6.40 nm for the SmA phase at 180°C. As shown in Table 4, the \( d_{10}/L \) value is 1.61, suggesting a bilayered organisation (SmA\(_2\)) with strong interdigitation of the alkyl chains. XRD analysis at SmC phase also indicates the bilayered organisation with an estimated tilt angle of around 25°.

As commented before, the nonionic compound CC-Dec was not synthesised in this study since its liquid crystalline behaviour was already described in the literature. As published by Van Hecke et al.,\[29\] the compound melts at 86°C to a SmC phase, changes to an SmA phase at 89°C, to the N phase at 95°C and the clearing point is observed at 101°C. It is important to note that, for the same compound, a different behaviour was observed by Pugh and Percec \[30\]. No decomposition temperature was described in both references. The last molecules synthesised in this work, the nonionic CC-Met and CaNN-Dec melts directly to the Iso state, do not show any liquid crystalline properties.

2.2.2.1. Influence of charges. According to the thermal and liquid crystalline data presented in Table 1, and as already described by other authors \[17,23,42\], a strong influence of charges in the calamitic liquid crystals is observed. Many nonionic compounds (XY-Dec and XY-Met) do not show any liquid crystalline behaviour, melting directly to the Iso, while their respective ionic compounds do show mesomorphic behaviour. This is even more evident for the CaNN class of compounds, which comprise an additional alkoxy chain, where both nonionic compounds melt directly to the liquid state. The additional alkoxy chain present in one side of the molecule provides a group bulky which hinders a molecular parallel packing and increases the excluded volume, inhibiting the liquid crystalline phase. However, in ILCs, the presence of charges promotes strong electrostatic interactions between the cations and anions and these strong noncovalent interactions partially compensate the unfavourable influence of the additional alkoxy chain, so that even the CaNN-10Br and CaNN-11 molecules show liquid crystalline behaviour.

As described in Table 1, NN-Dec and CC-Dec non-ionic show nematic phases besides smectic phases. However the nematic phase disappears when charges are added to the structure, as observed for the respective similar ionic compounds NN-10Br and NN-11. Thus, ionic electrostatic interactions tend to stabilise
lamellar phases rather than nematic [20], since the opposite charges tend to pack as closer as possible, favouring the formation layers of ions. Thus, the SmA phase is the most commonly observed for calamitic ILCs [2], as also observed for the molecules synthesised in this study. An increase of the mesophase stability is also observed for the ILCs. While the NN-Dec shows 6°C of mesophase range, NN-10Br and NN-8Im show 19°C and 88°C, respectively. However, CC-10Br shows a narrower range (9°C) in comparison with CC-Dec (15°C). This apparent controversy is caused by the lower decomposition temperatures normally observed for ILCs, as is the case of CC-10Br. Nevertheless, the imidazolium derivative CC-8Im shows a higher mesophase range (96°C) than CC-Dec. The presence of charges also promoted an increase of the melting points, this being more evident for the CC class of compound.

2.2.2.2. Additional alkoxy chain. The addition of a second long alkoxy chain in the structure of compounds NN, results in the molecules of the CaNN class. This additional bulky group brings some interesting properties modification, as already described before. For the nonionic azo molecules, the second alkoxy chain reduces the melting point temperature around 20°C. Besides, it extinguishes the liquid crystalline behaviour observed for NN-Dec. In both cases, the presence of the second bulky group hinders a proper molecular packing necessary for the liquid crystalline organisation and a strong crystalline structure.

For the ionic molecules, the addition of the second alkoxy chain leads to different variations of the thermal and liquid crystalline behaviour, which depends on the molecular structure. For the NN-10Br compound, the melting and clearing points are reduced by 33°C and 19°C, respectively. Therefore, the stronger decrease in the melting point results in an increase of the SmA phase stability. Interestingly, no modification of the molecular organisation in the SmA phase is observed.

Surprisingly, the addition of the second alkoxy chain in NN-1I structure resulting in CaNN-1I, promotes an increase of the melting point. Concerning the molecular organisation in the mesophase, a change from a bilayered smectic A phase (SmA₂) to an unknown MesX phase is observed. As already discussed before, the MesX phase could be a modulated bilayer SmA (SmA₂) or a columnar hexagonal phase (Colh), result of the significant difference between the volume fraction of the molecular sections. However, this cannot be surely confirmed from the obtained data. Recently, Butschies et al. described the mesomorphic behaviour for several molecules with amphiphilic shape similar to XY-1I but with a reduced core size, different ionic groups (acyclic and cyclic guanidinium and imidazolium) and a varied number of alkoxy chains [25]. They showed that molecules containing only one long aliphatic chain and a charge located at the end of the rigid core favoured a bilayered SmA organisation, similarly to what was described by us for NN-1I and CC-1I. Butschies also described that the molecules containing three long alkoxy chains resulted in columnar phases, while molecules with two alkoxy chains resulted in SmA or Colh phases, depending on the ionic unit. As suggested by Tschierske [22,23], this mesophase variation is already expected and related to the steric constraints from the additional chains. For the CaNN-11 compound, the larger core and the presence of the second chain suppress the SmA phase, favouring another molecular arrangement (SmA₂ or Colh). However, as commented before, no reliable conclusion can be drawn by our data.

The most interesting result is observed for the NN-8Im and CaNN-8Im compounds. Although only a small reduction of the melting point occurs, a significant change of the molecular polymorphism is observed. While a bilayered SmC and SmA phase was attributed to NN-8Im, a SmA₂ and a cubic phase are observed when an additional alkoxy chain is present. This polymorphic change can be explained by the increase of volume fraction of the alkoxy chains region. This promotes a disruption of the layers at lower temperatures and a curvature at higher temperatures, resulting in the modulated and cubic phases, respectively.

2.2.2.3. Position of the charge and chain length. As can be seen from Table 1, among the calamitic ionic liquid crystalline molecules of this study, modifications of the charge position or chain length result in significant modifications in the materials properties. No simple correlation between position of charges/chain length and the melting or clearing points can be drawn, since other factors seem to be additionally involved.

For the XY-10Br molecules, only a monolayer SmA phase is observed. At these molecules, the charge is placed at the end of the aromatic core and one long aliphatic chain is positioned on each side of the structure. Therefore, the only proper possibility to the molecules to pack together is through a side by side approximation, leading to the monolayer SmA phase. On the other hand, when the pyridinium aliphatic chain is reduced to its minimum (methyl group), the charge is practically at the end of the molecule. Therefore, the best electrostatic interaction is possible
when a head-to-head approximation of the molecules occur, leading to the bilayer SmA phase (or MesX for CaNN-11) with antiparallel organisation [22,23,37].

For the XY-8Im group, the charge is also located at the end of the molecular structure, but this time at the end of an alkoxy chain, far away from the rigid core (Figure 1). This helps the liquid crystalline stabilisation with respect to the other compounds where the charge is positioned at the rigid core periphery as noticed by the significant increase of the mesophase range for these compounds. It seems that in this case, an increase of intermolecular interactions (Coulombic and van der Waals) between the ionic, aromatic and aliphatic molecular sections favour the stability. Also, the position of the polar group results in an increment of the amphiphilic character (as for XY-11), promoting a head-to-head interaction of the polar units and favouring a bilayered structure.

Also, the presence of the imidazolium group as a polar head group promoted the stabilisation of SmC phases (SmC\textsubscript{e}) for the NN-8Im and CC-8Im compounds, behaviour which is seldom observed for ILCs [2]. For the CaNN-8Im compound similar behaviour could be observed, however the increase in the volume fraction of the apolar part promotes the change from the smectic to SmA and Cub phases as discussed before [22,23]. Although uncommon, Starkulla et al. demonstrated that SmC phases are stable for an ionic mesogens comprising a C\textsubscript{10} alkyl chain with C\textsubscript{8} spacer group and methylimidazolium end group, the main structure for the XY-8Im molecules of this study [37]. Also, Trbojevic et al. demonstrated that SmC phase can be favoured by increasing the alkyl chain length and decreasing the alkyl spacer length between the rigid core and the polar head group [21]. This not only favours the appearance of a SmC phase, but also the total liquid crystalline phase stability (mesophase range). On the other hand, Starkulla et al. also demonstrated a destabilisation of the SmC phase by increasing the N-alkyl substituent at the imidazolium cation [20,37].

2.2.2.4. Comparison of the linking group. Herein, we discuss the influence of the rigid core linking group. As already demonstrated by Cheng et al., changes in the linking group affect the thermal properties of the ILC [23]. Among the molecules synthesised in this work, a direct comparison can be made between the NN and CC groups. Both groups promote a molecular linearity, but the azo bond is known to be more flexible and somewhat withdraws the electrons density over the aromatic core (as can be observed by the higher chemical shifts of the \textsuperscript{1}H and \textsuperscript{13}C NMR peaks for the azo compounds). As described in Table 1, the variation of the thermal properties with the change of the linking group depends on the molecular structure of the compound. For the pyridinium ILCs, the change of N=N to C≡C bond promotes a significant increase of the melting point, but without changing the mesophase type. On the other hand, for the nonionic molecules, the same structural modification results in a decrease of the melting points. Besides, compound CC-Dec shows slightly higher mesophase stability (15°C against 6°C from NN-Dec) and the presence of a SmC phase, which is not observed for the similar azo compound. Interestingly, for the XY-8Im molecules, practically the same transition temperatures (and enthalpies), mesophases and liquid crystalline stability were observed for both linking groups. Therefore, we believe that for the XY-8Im molecules, the major responsible for the mesophase formation and its stabilisation is the presence and position of the imidazolium group, due to the electrostatic interactions promoted by its charges and counterions. A secondary factor is the van der Waals interactions between the rigid core and the aliphatic chains. The similar linearity of the core and the presence of the same aliphatic chains, do not seem to affect significantly the liquid crystalline behaviour in this case, since the Coulombic interactions are more important. The main difference between both materials is the temperature of the SmC\textsubscript{e}–SmA\textsubscript{2} transition, which is higher for the azo compound (NN-8Im). This agrees with the higher transitions observed for the azo compounds when no charge is localised in the rigid core (nonionic molecules discussed above).

Due the structure similarity, compounds of this study can be directly compared with the molecules synthesised by Westphal et al. [17], which comprise an 1,3,4-oxadiazol as linking unit. This heterocycle is known for its high lateral dipole moment, luminescence and to promote structure bend [26,27]. The data for the oxadiazole compounds are summarised in Table 5. As one may notice, the melting points for the oxadiazole derivatives are higher than the respective NN or CC molecules. The only exception is 1–1 (similar to XY-Met), which has basically the same melting point than NN-Met. The melting point of 1–1–1 is so high that thermal decomposition starts even before any other thermal transition is observed. The presence of the oxadiazol linking group also eliminates the SmC phase observed for the XY-8Im imidazolium derivatives and the liquid crystalline behaviour showed by the nonionic XY-Dec molecules. We believe that the oxadiazole bent-structure has major effect on this.

The oxadiazole compounds containing an additional alkoxy chains can be directly compared with the CaNN
3. Conclusions

In this study, we described the synthesis and complete characterisation of 14 ionic and nonionic molecules with several structural modifications. These compounds had their thermal stability and liquid crystalline behaviour complete investigated. Most of the compounds showed liquid crystalline properties with varied types of mesophases. We showed that each structural parameter investigated (presence of charges and its position, linking group, number of alkoxy chain and their length) affects intensely both thermal stability and liquid crystalline behaviour.

It was shown that the presence of ionic charges promoted a decrease of the thermal stability, especially for the pyridinium compounds. No significant thermal stability variation was found compounds containing an additional alkoxy chain, while the CC compounds shows a slightly higher thermal stability. However, all compounds synthesised in this work are less stable than the similar 1,3,4-oxadiazole derivatives already published in the literature.

Regarding liquid crystalline behaviour, a large influence of structure modifications over the transition temperatures and molecular organisation was confirmed. While the presence of charges favoured liquid crystalline behaviour, in special SmA phases, its position at the end of the molecular structure favoured bilayered smectic phases, stabilising even SmC organisation, which are seldom observed in ILCs. While the molecules with reduced alkoxy chains showed preference of SmA phases (and SmA2), the increased volume fraction caused by an additional alkoxy chain promoted layers modulation and ever it curvature, resulting in SmA and Cub phases, without significant changes to the mesophase stability. We also showed that the linking group (N=N or C≡C) affects the materials properties, but its effect is dependent of the molecular structure and on the presence of charges. However, these modifications are basically only related to transitions temperatures and not mesophases types. However, when comparison is made with oxadiazoles compounds, these variations are more significant, comprising the disappearance of mesophases and large melting point increase.

We believe that the results obtained in this work contribute to a deeper understanding of the thermotropic ILCs, especially in regard on how structural modifications of the mesogens will affect its properties and their molecular organisation. This knowledge is of fundamental importance in the search of more robust materials, with higher and better applicability.

4. Experimental section

4.1. Materials and characterisation

The main chemicals used in this study were: tetrafluorooboric acid (48%, Sigma-Aldrich), 4-aminopyridine (98%, Sigma-Aldrich), phenol (P.A. ACS, Chemistry Group), 1-bromodecane (97%, Sigma-Aldrich), iodomethane (99.5%, Sigma-Aldrich), 1,8-dibromooctane (98%, Sigma-Aldrich), catechol (≥99%, Sigma-Aldrich), tetrabutylammonium bromide (≥98%, Sigma-Aldrich), palladium on carbon (10%, Sigma-Aldrich), butyl nitrite (90%, Sigma-Aldrich), 2-methyl-3-butyn-3-ol (98%, Sigma-Aldrich), 1-methylimidazole (99%, Sigma-Aldrich). All other inorganic and organic compounds, including the solvents, were of the highest purity, purchased from commercial sources (Merck, Sigma-Aldrich, Fluka and Acros), and used as received. Dry solvents were used when specified. Dry TEA was obtained by distillation over KOH while dry THF was obtained by distillation over sodium. Thin layer chromatography (TLC) was carried out using silica gel Si 60-F254 (Merck). Purifications were carried out by recrystallisation using commercial grade solvents and by column chromatography on 60–200 mesh, 60A, silica gel (Acros). 1H and 13C NMR spectra were recorded with a Varian Mercury Plus spectrometer operating at 400 and 100.6 MHz, respectively, or with a Bruker AC-200F spectrometer operating at 200 and 50.4 MHz, respectively. High-resolution mass spectra were recorded on a Bruker microTOF-Q II mass spectrometer using the APPI (Atmospheric Pressure Photoionization) or ESI (electrospray ionization) ionisation method and operating in positive and negative ion modes.
4.2. Microwave reactions

The imidazolium ionic compounds were synthesised using a Discover system microwave (CEM). All reactions were performed in open-vessel mode by controlling the temperature at 90°C with an initial power of 50 W.

4.3. Thermal analysis

Melting points, thermal transitions and mesomorphic textures were determined using an Olympus BX50 microscope equipped with a Mettler Toledo FP-82 hot stage and an Olympus DP73 digital camera.

DSC was used to determine the thermal phase transitions and energy changes. A DSC Q2000 calorimeter (TA Instruments) equipped with a RCS90 cooling system was used and the DSC analysis was performed under nitrogen atmosphere (flow of 50 mL min⁻¹) with a heating/cooling rate of 10°C min⁻¹. Around 1–2 mg of material was placed in a non-hermetic closed aluminium pan, and an empty aluminium pan was used as the reference. The temperature range was selected according to MOLP results.

Thermal stability was investigated by TGA using a Shimadzu thermobalance with a TGA-50 module. The measurements were performed in platinum crucible, under a nitrogen flow of 20 mL min⁻¹. The temperature was varied from 30°C to 900°C with a heating rate of 10°C min⁻¹.

4.4. XRD analysis

The XRD analysis was carried out with the XPERT-PRO (PANalytical) diffractometer, using Cu Kα radiation (λ = 1.5418 Å), operated at 40 kV and 30 mA. The diffraction patterns were recorded in the 2θ range of 1.5–30° and the diffracted radiation collected with an X’Celerator detector using a nickel filter. Prior to the measurements, the samples were prepared by heating a certain amount of the desired compound on a glass plate, using a hot stage. The samples that did not decompose at the clearing point were heated to the liquid state. The samples that did decompose before reaching the clearing point were heated until a few degrees below the decomposition temperature. After heating, all samples were slowly cooled to room temperature. The glass plate containing the sample was then placed in the diffractometer chamber with a temperature control unit (TCU2000 – Anton Paar), which allowed control of the samples temperature during the measurements. The XRD measurements were performed during the heating process for the samples that decomposed easily, and on cooling from the isotropic phase for the samples that did not decompose before the clearing point.

4.5. Single crystal XRD

Suitable crystals of the compound CC-II were obtained through slow crystallisation from THF, with gravity filtering of the crystals. Crystallographic analysis was carried out at temperature of 173(2)K with a selected prismatic yellow crystal, which was mounted on a Bruker Kappa APEX II DUO diffractometer using graphite monochromated Mo Ka radiation (λ = 0.71073 Å). The frames were integrated with the Bruker SAINT software package [43]. All data were corrected for Lorentz and polarisation effects. The intensities were also corrected for absorption effects using the multi-scan method (SADABS) [44]. The structure was solved using direct methods with SIR-97 [45] and refined by full-matrix least-squares procedures on F² using SHELXL-97 [46]. H atoms bonded to C atoms were added at their calculated positions and included in the structure factor calculations, with C–H distances and Ueq taken from the default of the refinement program. Ortep plot was drawn using PLATON software [47]. Selected crystal data: C₄₈H₇₂I₂N₂O₆, M = 1026.88, triclinic, P-1, a = 8.4783(2) Å, b = 9.6426(2) Å, c = 16.8704(4) Å, α = 88.5240(10)°, β = 80.9730(10)°, γ = 65.4770(10)°, V = 1238.06(5) Å³, Z = 1, Dcalcd = 1.377 Mg/m³, μ = 1.316 mm⁻¹, F(000) = 528, unique 9436 (Rint = 0.0131), refined parameters = 264, Goof (F²) = 1.127, R1[I > 2σ(I)] = 0.0212, wR2 (all data) = 0.0562.

4.6. Synthesis

(E) 4-[(4-hydroxyphenyl)diazenyl]pyridine

(i) Diazotisation: A mixture of 4-aminopyridine (1) (4.00 g, 42.5 mmol) with 35 mL of tetrafluoroboric acid (48 wt% in H₂O) was cooled to −5°C in an ice/NaCl/acetone bath and NaNO₂ (3.08 g, 44.6 mmol) was added in small portions over 45 min under intense stirring. After complete addition, the sample was maintained in the cold bath for a further 1 h and the suspension was then filtered by vacuum filtration and was dried, yielding the diazonium salt. ¹H NMR (DMSO-d₆ − 200 MHz) δ ppm: 7.26 (d, J = 7.2 Hz, 2H, Py−H), 8.57 (d, J = 7.2 Hz, 2H, Py−H).

(ii) Azo-coupling: To 300 mL of an aqueous solution containing phenol (4.00 g, 42.5 mmol) and NaOH (4.08 g, 102 mmol) at room temperature, the freshly prepared diazonium salt was added in small portions,
resulting in a strong red solution. After complete addition, the mixture was stirred for a further 30 min. The pH was adjusted to 7 and the precipitate formed was collected by filtration and washed with water. The product was purified by recrystallisation over DMF/H₂O, yielding 6.68 g (79% after the two steps) of a reddish solid. m.p.: 253.8–256.0°C (lit. 265°C) [48].¹H NMR (DMSO-d₆ – 400 MHz) δ ppm: 6.96 (d, J = 6.8 Hz, 2H, Ar–H), 7.66 (d, J = 4.5 Hz, 2H, Py–H), 7.86 (d, J = 6.8 Hz, 2H, Ar–H), 8.75 (d, J = 4.5 Hz, 2H, Py–H), 10.59 (s, 1H, Ar–OH).¹³C NMR (DMSO-d₆ – 100 MHz) δ ppm: 116.46, 116.86, 126.47, 145.91, 152.01, 157.48, 162.99.

(E)-4-[(4-decyloxyphenyl)diazenyl]-1-methylpyridinium iodide (NN-II)

In a round-bottomed flask were added (E)-4-[(4-decyloxyphenyl)diazenyl]pyridine (2) (0.80 g, 2.36 mmol), iodomethane (0.74 mL, 11.8 mmol) and acetonitrile (40 mL), the mixture was heated to 70°C and stirred for 20 h. The solution was cooled to room temperature and the solvent and excess of iodomethane removed under reduced pressure. The azo ionic compound was purified by maceration in boiling heptane, yielding 1.09 g (96%) as a dark red solid. m.p.: (see Table 1).¹H NMR (CDCl₃ – 400 MHz) δ ppm: 0.89 (t, J = 6.9 Hz, 3H, –CH₃), 1.20–1.40 (m, 12H, –CH₂–), 1.49 (m, 2H, –CH₂–), 1.84 (m, 2H, –CH₂CH₂O–), 4.09 (t, J = 6.6 Hz, 2H, –CH₂O–), 4.74 (s, 3H, Py⁺–CH₃), 7.03 (d, J = 9.1 Hz, 2H, Ar–H), 8.00 (d, J = 9.1 Hz, 2H, Ar–H), 8.24 (d, J = 7.0 Hz, 2H, Py–H), 9.45 (d, J = 7.0 Hz, 2H, Py–H).¹³C NMR (CDCl₃ – 100 MHz) δ ppm: 14.37, 22.90, 26.16, 29.24, 29.53, 29.56, 29.77, 32.11, 49.28, 69.19, 115.69, 120.31, 127.99, 147.28, 147.64, 161.04, 165.82. Q-TOF MS/ESI: m/z calc for C₂₂H₂₃N₂O [M⁺]: 354.2540; found: 354.2541. Q-TOF MS/ESI: m/z calc for Γ: 126.9050; found: 126.9036.

4-decyloxyacetanilide

In a round-bottomed flask were added 4-hydroxyacetanilide (3) (5.00 g, 33.1 mmol), 1-bromodecane (8.2 mL, 93.7 mmol), K₂CO₃ (9.14 g, 66.2 mmol) and 100 mL of butanone. The suspension was refluxed for 20 h. The suspension was then filtered and washed two times with hot butanone and the solvent was removed by evaporation under reduced pressure. The crude product was recrystallised from heptane, affording 9.63 g of a white solid (99%). m.p.: 88.0–89.0°C.¹H NMR (CDCl₃ – 200 MHz) δ ppm: 0.88 (t, J = 6.7 Hz, 3H, –CH₃), 1.25–1.35 (m, 12H, –CH₂–), 1.43 (m, 2H, –CH₂–), 1.76 (m, 2H, –CH₂CH₂O–), 2.14 (s, 3H, –COCH₃), 3.91 (t, J = 6.6 Hz, 2H, –CH₂O–), 6.83 (d, J = 9.0 Hz, 2H, Ar–H), 7.27 (br, 1H, Ar–NH–), 7.36 (d, J = 9.0 Hz, 2H, Ar–H).¹³C NMR (CDCl₃ – 100 MHz) δ ppm: 14.10, 22.66, 25.96, 29.10, 29.29, 29.34, 29.53, 31.87, 68.47, 114.83, 116.12, 125.56, 146.63, 151.17, 157.40, 162.88.

(E)-1-decyl-4-[(4-decyloxyphenyl)diazenyl]pyridinium iodide (NN-1Br)

The following reagents were added to a round-bottomed flask: 4-[(4-decyloxyphenyl)diazenyl]pyridine (2) (0.80 g, 2.36 mmol), 1-bromodecane (0.98 mL, 4.27 mmol) and acetonitrile (30 mL). The mixture was refluxed for 2 days. The solution was cooled to room temperature and it poured into 300 mL of ethyl ether, was filtered and washed with more ether, affording 1.13 g (86%) of the pure red product. m.p.: (see Table 1).¹H NMR (CDCl₃ – 400 MHz) δ ppm: 0.85 (m, 6H, –CH₃), 1.15–1.43 (m, 26H, –CH₂–), 1.47 (m, 2H, –CH₂–), 1.83 (m, 2H, –CH₂CH₂O–), 2.04 (m, 2H, –CH₂CH₂Py⁺–), 4.07 (t, J = 6.5 Hz, 2H, –CH₂O–), 5.01 (t, J = 7.3 Hz, 2H, Py⁺CH₂–), 7.01 (d, J = 9.2 Hz, 2H, Ar–H), 7.98 (d, J = 9.2 Hz, 2H, Ar–H), 8.22 (d, J = 7.0 Hz, 2H, Py–H), 9.56 (d, J = 7.0 Hz, 2H, Py–H).¹³C NMR (CDCl₃ – 100 MHz) δ ppm: 14.34, 14.36, 22.87, 22.90, 26.16, 26.33, 29.24, 29.34, 29.46, 29.53, 29.56, 29.59, 29.67, 29.77, 32.03, 32.11, 32.29, 61.71, 69.18, 115.67, 120.37, 127.90, 147.03, 147.29, 161.05, 165.80. Q-TOF MS/ESI: m/z calc for C₃₉H₅₀N₄O [M⁺]: 480.3948; found: 480.3945. Q-TOF MS/ESI: m/z calc for Br⁺: 78.9189; found: 78.9171.

4-decyloxyaniline (4)

In a round-bottomed flask, 4-decyloxyacetanilide (3) (9.44 g, 32.4 mmol), 100 mL of H₂O and 200 mL of methanol were added and heated at 80°C. After complete solubilisation, 30 mL of concentrated
hydrochloric acid was slowly and carefully added, maintaining the temperature at 80°C for 20 h. After this period, part of the methanol was removed under reduced pressure and the remaining solution was basified with NaOH aqueous solution (20%). The resulting solid was filtered and washed with plenty of water. The solid obtained was air-dried and was already pure enough for the next reaction step, affording 7.96 g (98%). m.p.: 47.0-47.5°C. 1H NMR (CDCl3 – 200 MHz) δ ppm: 0.88 (t, J = 6.7 Hz, 3H, CH3), 1.25–1.35 (m, 12H, –CH2–), 1.43 (m, 2H, –CH2–), 1.73 (m, 2H, –CH2CH2O–), 3.87 (t, J = 6.6 Hz, 2H, –CH2O–), 6.63 (d, J = 8.6 Hz, 2H, Ar–H), 6.75 (d, J = 8.6 Hz, 2H, Ar–H). 13C NMR (CDCl3 – 100 MHz) δ ppm: 14.37, 22.93, 26.32, 29.58, 29.69, 29.82, 29.85, 32.15, 68.95, 115.82, 116.75, 140.00, 152.68.

(E)-4-[(4-decyloxyphenyl)diazenyl]phenol (5)

(i) Diazonium salt: 4-decyloxyaniline (4) (3.00 g, 12.05 mmol), HBF4 (48%) (15 mL) and 40 mL of diethyl ether were added to a 100 mL round-bottomed flask, and then cooled to 0°C with an ice/NaCl bath. NaN3 (0.91 g, 13.26 mmol) was then slowly added to the reaction for 60 min and after, was stirred at 0°C for another 60 min. The resulting precipitate was filtered in a Buchner funnel, yielding the diazonium salt as a light grey solid. 1H NMR (CDCl3 + DMSO-d6 – 200 MHz) δ ppm: 0.88 (t, J = 6.7 Hz, 3H, CH3), 1.22–1.48 (m, 14H, –CH2–), 1.83 (m, 2H, –CH2CH2O–), 4.17 (t, J = 6.5 Hz, 2H, –CH2O–), 7.18 (d, J = 9.4 Hz, 2H, Ar–H), 8.51 (d, J = 9.4 Hz, 2H, Ar–H).

(ii) Azo-coupling: Phenol (1.13 g, 12.05 mmol) and NaOH (0.96 g, 24.10 mmol) were added to a beaker and dissolved in 300 mL of water. Under strong stirring at room temperature, the solid diazonium salt was slowly added to the basic phenol solution. After complete addition, the solution was stirred for further 3 h. After this period, the pH was adjusted to 3 with an HCl 10% solution and the product was extracted with ethyl acetate (3 × 100 mL). The combined organic phase was dried over anhydrous Na2SO4 and the solvent removed under reduced pressure. The crude solid was purified by silica gel column chromatography using hexane/ethyl acetate (9:1) as eluent, affording 2.73 g (65%) of a reddish solid. m.p.: 98.8–100.7°C. 1H NMR (CDCl3 + DMSO-d6 – 400 MHz) δ ppm: 0.88 (t, J = 6.7 Hz, 3H, –CH3), 1.18–1.38 (m, 12H, –CH2–), 1.46 (m, 2H, –CH2–), 1.80 (m, 2H, –CH2CH2O–), 4.02 (t, J = 6.6 Hz, 2H, –CH2O–), 6.95 (d, J = 8.8 Hz, 2H, Ar–H), 6.97 (d, J = 9.0 Hz, 2H, Ar–H), 7.78 (d, J = 8.9 Hz, 2H, Ar–H), 7.83 (d, J = 9.0 Hz, 2H, Ar–H), 9.36 (s, 1H, Ar–OH). 13C NMR (CDCl3 + DMSO-d6 – 100 MHz) δ ppm: 14.13, 22.65, 25.98, 29.19, 29.28, 29.35, 29.52, 29.62, 31.86, 68.29, 114.61, 115.89, 124.11, 124.42, 146.18, 146.85, 159.96, 160.64.

(E)-1,2-bis(4-decyloxyphenyl)diazone (NN-Dec)

To a round-bottomed flask were added 4-[(4-decyloxyphenyl)diazenyl]phenol (5) (0.50 g, 1.41 mmol), 1-bromodecane (0.35 mL, 1.69 mmol), K2CO3 (0.39 g, 2.82 mmol) and 30 mL of butanone. The mixture was refluxed under stirring for 20 h, cooled to room temperature, filtered and washed with chloroform. The crude product, obtained after removal of the solvent, was purified by silica gel column chromatography using a chloroform/hexanes (1:1) as eluent, affording 0.64 g (93%). m.p.: (see Table 1). 1H NMR (CDCl3 – 400 MHz) δ ppm: 0.89 (t, J = 6.8 Hz, 6H, –CH3), 1.18–1.40 (m, 24H, –CH2–), 1.47 (m, 4H, –CH2–), 1.81 (m, 4H, –CH2CH2O–), 4.03 (t, J = 6.6 Hz, 4H, –CH2O–), 6.99 (d, J = 9.0 Hz, 4H, Ar–H), 7.86 (d, J = 9.0 Hz, 4H, Ar–H). 13C NMR (CDCl3 – 100 MHz) δ ppm: 14.37, 22.93, 26.26, 29.45, 29.56, 29.63, 29.80, 29.82, 32.14, 68.55, 114.87, 124.51, 147.14, 161.35. Q-TOF MS/APPI: m/z calcd for C38H35N2O2 [M + H]+: 549.3945; found: 549.3948.

(E)-1-[(4-decyloxyphenyl)-2-(4-methoxyphenyl)diazone (NN-Met)

To a round-bottomed flask were added 4-[(4-decyloxyphenyl)diazenyl]phenol (5) (0.50 g, 1.41 mmol), iodomethane (0.27 mL, 4.23 mmol), K2CO3 (0.39 g, 2.82 mmol) and 30 mL of acetone. The mixture was heated to 50°C and stirred for 20 h. After this period, the suspension was cooled to room temperature, filtered and washed with chloroform. The crude product, obtained after removal of the solvent, was purified by silica gel column chromatography using a chloroform/hexanes (1:1) as eluent, affording 0.48 g (92%). m.p.: (see Table 1). 1H NMR (CDCl3 – 400 MHz) δ ppm: 0.89 (t, J = 6.8 Hz, 3H, –CH3), 1.20–1.39 (m, 12H, –CH2–), 1.48 (m, 2H, –CH2–), 1.82 (m, 2H, –CH2CH2O–), 3.88 (s, 3H, –OCH3), 4.02 (t, J = 6.6 Hz, 2H, –CH2O–), 6.99 (d, J = 9.0 Hz, 2H, Ar–H), 7.00 (d, J = 9.0 Hz, 2H, Ar–H), 7.87 (d, J = 9.0 Hz, 2H, Ar–H), 7.88 (d, J = 9.0 Hz, 2H, Ar–H). 13C NMR (CDCl3 – 100 MHz) δ ppm: 14.37, 22.93, 26.26, 29.45, 29.56, 29.63, 29.80, 29.82, 32.14, 55.75, 68.56, 114.37, 114.88, 124.53, 147.11, 147.32, 161.43, 161.71. Q-TOF MS/APPI: m/z calcd for C32H29N2O2 [M + H]+: 481.25365; found: 481.25374.

(E)-1-[4-(8-bromo-octyloxy)phenyl]-2-(4-decyloxyphenyl)diazene (36)

A mixture of (E)-4-[(4-decyloxyphenyl)diazenyl] phenol (5) (1.50 g, 4.23 mmol), 1,8-dibromo-octane (2.3 mL, 12.7 mmol), K2CO3 (1.17 g, 8.46 mmol) and 100 mL butanone were added to a round-bottomed flask, heated at 70°C and stirred for 20 h. The
suspension was filtered hot, washed with chloroform and the solvent removed under reduced pressure. The crude product was recrystallised with hexane, affording 1.81 g (78%) of the pure compound. m.p.: Cr − 93°C − SmA − 111°C − Iso. 1H NMR (CDCl3 − 400 MHz) δ ppm: 0.88 (t, J = 6.6 Hz, 3H, −CH3), 1.20–1.55 (m, 22H, −CH2−), 1.77–1.91 (m, 6H, −CH2−), 3.42 (t, J = 6.8 Hz, 2H, −CH2Br), 4.03 (t, J = 6.5 Hz, 4H, −CH2O−), 6.98 (d, J = 9.0 Hz, 4H, Ar−H), 7.86 (d, J = 9.0 Hz, 4H, Ar−H). 13C NMR (CDCl3 − 100 MHz) δ ppm: 14.38, 22.93, 26.17, 26.26, 28.32, 28.92, 29.40, 29.42, 29.25, 29.56, 29.63, 29.80, 29.82, 32.14, 33.00, 34.27, 68.44, 68.55, 114.87, 124.51, 147.11, 147.15, 161.31, 161.39.

(E)-2-(4-decyloxyphenyl)-1-[4-(8-methyl-3-imidazolium)octyloxy]phenyl)diazenyl bromide (NN-81m)

To a 25 mL round-bottomed flask equipped with a condenser were added (E)-1-[4-(8-bromooclyoxy)phenyl]-2-(4-decyloxyphenyl)diazenyl (6) (1.00 g, 1.83 mmol) and 15 mL of 1-methylimidazole. The mixture was irradiated in a microwave oven for two periods of 5 min each (temperature of 90°C with an initial power of 50 W). The suspension was then poured into 300 mL of diethyl ether and filtered. The crude product was purified by silica gel column chromatography using a chloroform/methanol gradient as eluent (from 100:0 until 9:1), affording 0.99 g (86%) of the pure compound. m.p.: (see Table 1). 1H NMR (CDCl3 − 400 MHz) δ ppm: 0.88 (t, J = 6.8 Hz, 3H, −CH3), 1.17–1.50 (m, 22H, −CH2−), 1.79 (m, 4H, −CH2CH2O−), 1.91 (m, 2H, Im−CH2−), 4.01 (t, J = 6.6 Hz, 2H, −OCH2−), 4.02 (t, J = 6.6 Hz, 2H, −OCH2−), 4.10 (s, 3H, Im−CH3), 4.31 (t, J = 7.4 Hz, 2H, Im−CH2−), 6.98 (d, J = 9.0 Hz, 2H, Ar−H), 6.99 (d, J = 9.0 Hz, 2H, Ar−H), 7.35 (t, J = 1.7 Hz, 1H, Im−H), 7.46 (t, J = 1.7 Hz, 1H, Im−H), 7.85 (d, J = 9.0 Hz, 2H, Ar−H), 7.86 (d, J = 9.0 Hz, 2H, Ar−H), 10.37 (s, 1H, Im−H). 13C NMR (CDCl3 − 100 MHz) δ ppm: 14.37, 22.91, 26.07, 26.24, 26.36, 29.09, 29.26, 29.31, 29.43, 29.54, 29.62, 29.78, 30.47, 32.12, 36.95, 50.35, 68.36, 68.55, 114.88, 121.95, 123.60, 124.49, 137.81, 147.04, 147.10, 161.29, 161.41. Q-TOF MS/ESI: m/z calc'd for C34H51N2O2 [M]+: 547.4007; found: 547.4001. Q-TOF MS/ESI: m/z calc'd for Br−: 78.9189; found: 78.9176.

2-decyloxyphenol (8)

Catechol (7) (5.5 g, 50 mmol), 1-bromodecane (12.8 g, 58 mmol) and K2CO3 (5.5 g, 55 mmol) were added to a 250 mL round-bottomed flask, followed by DMF (10 mL). Reaction was heated to 95°C and stirred for 8 h. The suspension was poured in cold water (200 mL) and extracted with chloroform (3 × 100 mL). Solvent was evaporated under reduced pressure. Crude solid was purified by silica gel column chromatography with hexane/CH2Cl2 (9:1) as eluent, yielding 12.5 g (52%) of the product was obtained. m.p.: liquid at room temperature. 1H NMR (CDCl3 − 400 MHz) δ ppm: 0.88 (t, J = 6.8 Hz, 3H, −CH3), 1.23–1.36 (m, 12H, −CH2−), 1.45 (m, 2H, −CH2−), 1.81 (m, 2H, −CH2CH2O), 4.03 (t, J = 6.6 Hz, 2H, −CH2O), 5.66 (s, 1H, Ar−OH), 6.86–7.02 (m, 4H, Ar−H). 13C NMR (CDCl3 − 100 MHz) δ ppm: 14.11, 22.68, 26.02, 29.25, 29.31, 29.38, 29.55, 29.57, 31.89, 68.87, 111.59, 114.42, 120.04, 121.26, 145.82, 145.96.

(E)-2-(decyloxy)-5-((pyridin-4-yl)diazenyl)phenol (9):

(i) Diazonium salt: To a 100 mL round-bottomed flask, 4-aminopyridine (1) (1.60 g, 17.0 mmol) was added, dissolved in HBF4 (14 mL) and the solution cooled at −5°C with ice/NaCl bath. NaNO2 (1.29 g, 18.7 mmol) was then slowly added to the reaction for a period of 30 min. After another 30 min of stirring, the precipitate was filtered in a Büchner funnel, yielding the diazonium salt as an off-white solid.

(ii) Azo-coupling: In a beaker, 2-decyloxyphenol (8) (3.90 g, 15.6 mmol) and TEA (8 mL) were dissolved in 100 mL of THF, and the solution cooled to 5°C. The diazonium salt was then slowly added to the solution under stirring. The reaction was maintained at 5°C for 1 h and at room temperature for further 20 h. The solvent was evaporated under reduced pressure, water (150 mL) was added to the flask and the pH was adjusted to =6 using a HCl 10% solution. The product was extracted with ethyl acetate (3 × 100 mL). The organic phase was dried with anhydrous Na2SO4 and the solvent removed under reduced pressure. Crude solid was purified over silica gel column chromatography, using CHCl3/ethyl acetate gradient as eluent (from 100:0 to 97:3), affording 0.73 g (13%) of a red solid (2.79 g of 2-decyloxyphenol was recovered). m.p.: 113.7–114.3°C. 1H NMR (CDCl3 − 400 MHz) δ ppm: 0.88 (t, J = 6.8 Hz, 3H, −CH3), 1.22–1.40 (m, 12H, −CH2−), 1.48 (m, 2H, −CH2−), 1.87 (m, 2H, −CH2CH2O−), 4.16 (t, J = 6.6 Hz, 2H, −CH2O), 6.30 (br, 1H, Ar−OH), 7.09 (d, J = 8.6 Hz, 1H, Ar−H), 7.49 (d, J = 2.0 Hz, 1H, Ar−H), 7.66 (dd, J = 8.6 Hz and J = 2.0 Hz, 1H, Ar−H), 7.68 (d, J = 5.0 Hz, 2H, Py−H), 8.77 (d, J = 5.0 Hz, 2H, Py−H). 13C NMR (CDCl3 − 100 MHz) δ ppm: 14.11, 22.67, 25.99, 29.04, 29.30, 29.34, 29.54, 31.87, 69.15, 102.49, 114.42, 116.22, 123.06, 146.48, 146.82, 150.69, 151.00, 157.47.

(E)-4-[3,4-bis(decyloxy)phenyl]diazenylpyridine (10)

To a 125 mL round-bottomed flask were transferred the 2-(decyloxy)-5-(pyridin-4-yl)diazenyl)phenol (9)
(0.80 g, 2.24 mmol), 1-bromodecane (0.49 g, 2.24 mmol) and K₂CO₃ (0.62 g, 4.48 mmol) and dissolved in butanone (50 mL). The reaction was then heated to 75°C and stirred for 24 h. The system was cooled to room temperature, filtered, evaporated under reduced pressure. Crude solid was purified over silica gel column chromatography, using CH₂Cl₂ as eluent, affording 0.730 g (67%) of the pure product. m.p.: 74.5–74.9°C. ¹H NMR (CDCl₃ – 200 MHz) δ ppm: 0.88 (t, J = 6.9 Hz, 6H, CH₃), 1.23–1.58 (m, 28H, –CH₂–), 1.88 (m, 4H, –CH₂CH₂O–), 4.10 (m, 4H, –CH₂O–), 7.00 (d, J = 8.8 Hz, 1H, Ar–H), 7.49 (d, J = 2.2 Hz, 1H, Ar–H), 7.66 (m, 3H, Ar–H), 8.77 (d, J = 5.8 Hz, 2H, Py–H).

(E)-4-[3,4-bis(decyloxy)phenyl]diazcneryl-1-decylpyridin-1-ium bromide (CaNN-10Br)

In a round-bottomed flask were added (E)-4-[3,4-bis (decyloxy)phenyl]diazcnerylpyridine (10) (0.26 g, 0.52 mmol), 1-bromodecane (0.34 g, 1.56 mmol) and acetonitrile (10 mL). The mixture was heated to 90°C, stirred for 2 days, cooled to room temperature, and the solvent removed under reduced pressure. The crude ionic product was purified by silica column chromatography using ethyl acetate/methanol gradient as eluent (from 100:0 until 95:5). The purified product was dissolved in the minimum volume of chloroform, 80 mL of hexane were added and the resulting precipitate filtered, affording 0.27 g (73%) of a red solid. m.p.: (see Table 1). ¹H NMR (CDCl₃ – 200 MHz) δ ppm: 0.88 (m, 9H, –CH₃), 1.19–1.57 (m, 42H, –CH₂–), 1.87 (m, 4H, –CH₂CH₂O–), 2.05 (m, 2H, –CH₂CH₂Py⁺–), 4.07 (t, J = 6.6 Hz, 2H, –OCH₂–), 4.14 (t, J = 6.6 Hz, 2H, –OCH₂–), 5.01 (t, J = 7.0 Hz, 2H, Py⁺–CH₂–), 7.01 (d, J = 8.6 Hz, 1H, Ar–H), 7.45 (d, J = 2.2 Hz, 1H, Ar–H), 7.75 (dd, J = 8.6 Hz and J = 2.2 Hz, 1H, Ar–H), 8.24 (d, J = 6.8 Hz, 2H, Py–H), 9.50 (d, J = 6.8 Hz, 2H, Py–H). ¹³C NMR (CDCl₃ – 50 MHz) δ ppm: 13.98, 22.53, 22.57, 25.85, 25.96, 26.03, 28.87, 28.96, 29.02, 29.12, 29.25, 29.31, 29.34, 29.44, 29.49, 29.52, 31.72, 31.81, 31.94, 61.28, 69.15, 69.41, 102.58, 111.71, 120.01, 127.34, 146.80, 147.15, 150.03, 156.41, 160.83. Q-TOF MS/ESI: m/z calc for C₄₂H₃₂N₂O₂ [M⁺]: 510.4054; found: 510.4055. Q-TOF MS/ESI: m/z calc for Γ: 126.9050; found: 126.9038.

1,2-bis(decyloxy)benzene:

To a 500 mL round-bottomed flask were transferred the catechol (4 g, 36.4 mmol), 1-bromodecane (17.6 g, 80 mmol), K₂CO₃ (20.1 g, 145.6 mmol) and catalytic amounts of TBAB, followed by dissolution in butanone (150 mL). The reaction was stirred for 24 h at 95°C and after, it was cooled to room temperature. The organic phase was filtered and concentrated under reduced pressure. The crude solid was recrystallised with ethanol, affording 13.4 g (94%) of the pure product. m.p.: 37.9 – 38.9°C (lit: 41°C) [50]. ¹H NMR (CDCl₃ – 400 MHz) δ ppm: 0.89 (t, J = 6.3 Hz, 6H, CH₃), 1.20–1.42 (m, 42H, –CH₂–), 1.47 (m, 4H, –CH₂–), 1.82 (m, 4H, –CH₂CH₂O–), 4.00 (t, J = 6.6 Hz, 4H, –CH₂O–), 6.90 (s, 4H, Ar–H). ¹³C NMR (CDCl₃ – 100 MHz) δ ppm: 14.12, 22.69, 26.05, 29.36, 29.44, 29.59, 29.64, 31.91, 69.25, 114.04, 120.96, 149.20.

1,2-bis(decyloxy)-4-nitrobenzene:

1,2-bis(decyloxy)benzene (2.63 g, 6.75 mmol) was weighted in a two-necked round-bottomed flask, dissolved in a small quantity of CH₂Cl₂ (12 mL), followed by addition of NaN₂O₃ (0.066 g, 0.96 mmol). The reaction was then stirred and cooled to –2°C with NaCl/ice bath and HNO₃ (1.4 mL, 20.25 mmol) was added dropwise to the solution. After the acid was added, reaction was stirred for 1 h at room temperature. 100 mL of water was added and the system was extracted with 3 × 30 mL of CH₂Cl₂. The combined organic phase was washed with 60 mL of NaHSO₄, dried with anhydrous Na₂SO₄ and the solvent removed under reduced pressure. The crude product was purified by recrystallisation with ethanol, affording 2.61 g (89%) of a pale yellow solid. m.p.: 70.1–70.3°C (lit: 69–71°C) [51]. ¹H NMR (CDCl₃ – 400 MHz) δ ppm: 0.88 (t, J = 6.0 Hz, 6H, CH₃), 1.21–1.35 (m, 24H, –CH₂–), 1.48 (m, 4H, –
CH₃–), 1.85 (m, 4H, –CH₂CH₂O–), 4.05 (t, J = 6.7 Hz, 2H, –CH₂O–), 4.08 (t, J = 6.7 Hz, 2H, –CH₂O–), 6.88 (d, J = 9.0 Hz, 1H, Ar–H), 7.73 (d, J = 2.7 Hz, 1H, Ar–H), 7.88 (dd, J = 2.7 Hz and 9.0 Hz, 1H, Ar–H). ¹³C NMR (CDCl₃ – 100 MHz) δ ppm: 14.09, 22.67, 25.89, 28.93, 29.33, 29.56, 31.89, 69.39, 69.43, 108.00, 110.97, 117.63, 141.13, 148.62, 154.66.

3,4-bis(decyloxy)aniline (11)

1,2-bis(decyloxy)-4-nitrobenzene (3.54 g, 8.13 mmol) was dissolved in THF (15 mL) and methanol (1 mL) and transferred to a reactor. A catalytic amount of Pd/C 10% was then added to the mixture. 120 psi of H₂ was applied at the suspension for 5 h with stirring. The reaction was filtered through celite, the solvent was evaporated under reduced pressure and the crude solid was recrystallised with methanol, giving 2.90 g (90%) of a pink solid. m.p.: 44–45°C (lit: 47–49°C) [51]. ¹H NMR (CDCl₃ – 200 MHz) δ ppm: 0.88 (t, J = 6.3 Hz, 6H, CH₃), 1.17–1.56 (m, 28H, –CH₂–), 1.79 (m, 4H, –CH₂CH₂O–), 3.93 (m, 4H, –CH₂O), 6.22 (dd, J = 2.4 Hz and J = 8.2 Hz, 1H, Ar–H), 6.32 (d, J = 2.4 Hz, 1H, Ar–H), 6.73 (d, J = 8.2 Hz, 1H, Ar–H). ¹³C NMR (CDCl₃ – 50 MHz) δ ppm: 14.08, 22.65, 26.03, 29.32, 29.56, 31.88, 68.89, 70.90, 102.56, 106.76, 117.24, 141.12, 150.53, 190.84.

(E)-4-[3,4-bis(decyloxy)phenyl]diazene (CaNN-Dec)

In a 50 mL round-bottomed flask, (E)-4-[3,4-bis(decyloxy)phenyl]diazene (12) (0.21 g, 0.41 mmol) was transferred, dissolved in butanone (10 mL), followed by addition of 1-bromodecane (0.27 g, 1.23 mmol) and K₂CO₃ (0.11 g, 0.82 mmol). Reaction was stirred for 24 h at 50°C. The suspension was cooled to room temperature, filtered and solvent was removed under reduced pressure. The crude solid was purified with silica gel column chromatography, using hexane/ethyl acetate (9:1) as eluent, affording 0.27 g (90%) of a yellow solid. m.p.: 105.1–105.8°C. ¹H NMR (CDCl₃ – 400 MHz) δ ppm: 0.89 (t, J = 6.3 Hz, 6H, –CH₃), 1.19–1.41 (m, 28H, –CH₂–), 1.48 (m, 4H, CH₂CH₂O–), 4.09 (m, 4H, –CH₂O), 6.06 (s, 1H, Ar–OH), 6.92 (d, J = 8.8 Hz, 2H, Ar–H), 6.98 (d, J = 8.4 Hz, 1H, Ar–H), 7.48 (d, J = 2.0 Hz, 1H, Ar–H), 7.54 (dd, J = 8.4 Hz and J = 2.0 Hz, 1H, Ar–H), 7.83 (d, J = 8.8 Hz, 2H, Ar–H). ¹³C NMR (CDCl₃ – 100 MHz) δ ppm: 14.11, 29.07, 29.38, 29.56, 31.90, 69.09, 69.23, 104.04, 112.29, 115.79, 119.80, 124.50, 146.83, 146.96, 149.35, 151.40, 157.99.

(A)-1-(3,4-bis(decyloxy)phenyl)-2-(4-decyloxy)phenyl)diazene (CaNN-Met)

In a 50 mL round-bottomed flask, (E)-4-[3,4-bis(decyloxy)phenyl]diazene (12) (0.23 g, 0.47 mmol) was transferred, dissolved in acetonitrile (10 mL), followed by addition of iodomethane (0.20 g, 1.41 mmol) and K₂CO₃ (0.13 g, 0.94 mmol). The reaction was stirred for 24 h at 50°C. Suspension was then cooled to room temperature, filtered and the solvent was removed under reduced pressure. The crude solid was purified with silica gel column chromatography, using hexane/ethyl acetate (9:1) as eluent, affording 0.27 g (90%) of a yellow solid. m.p.: 105.1–105.8°C. ¹H NMR (CDCl₃ – 400 MHz) δ ppm: 0.89 (t, J = 6.3 Hz, 6H, –CH₃), 1.19–1.41 (m, 28H, –CH₂–), 1.48 (m, 4H, CH₂CH₂O–), 4.09 (m, 4H, –CH₂O), 6.06 (s, 1H, Ar–OH), 6.92 (d, J = 8.8 Hz, 2H, Ar–H), 6.98 (d, J = 8.4 Hz, 1H, Ar–H), 7.48 (d, J = 2.0 Hz, 1H, Ar–H), 7.54 (dd, J = 8.4 Hz and J = 2.0 Hz, 1H, Ar–H), 7.83 (d, J = 8.8 Hz, 2H, Ar–H). ¹³C NMR (CDCl₃ – 100 MHz) δ ppm: 14.11, 29.07, 29.38, 29.56, 31.90, 69.09, 69.23, 104.04, 112.29, 115.79, 119.80, 124.50, 146.83, 146.96, 149.35, 151.40, 157.99.
chromatography, using hexane/CH₂Cl₂ gradient as eluent (from 100:0 to 50:50), affording 0.24 g (92%) of a yellow solid. m.p.: (see Table 1). ¹H NMR (CDCl₃ – 400 MHz) δ ppm: 0.90 (t, J = 6.8 Hz, 6H, –CH₃), 1.57–1.16 (m, 28H, –CH₂–), 1.88 (m, 4H, –CH₂CH₂O), 3.89 (s, 3H, –CH₃), 4.08 (t, J = 6.6 Hz, 2H, –CH₂O), 4.10 (t, J = 6.4 Hz, 2H, –CH₂O), 6.97 (d, J = 8.1 Hz, 1H, Ar–H), 7.01 (d, J = 9.0 Hz, 2H, Ar–H), 7.48 (d, J = 1.6 Hz, 1H, Ar–H), 7.53 (dd, J = 8.1 and 1.6 Hz, 1H, Ar–H) 7.89 (d, J = 9.0 Hz, 2H, Ar–H). ¹³C NMR (CDCl₃ – 100 MHz) δ ppm: 14.11, 22.69, 26.00, 26.04, 29.17, 29.35, 29.42, 29.58, 29.62, 29.63, 29.69, 31.91, 55.53, 69.04, 69.20, 104.11, 112.33, 114.13, 119.67, 124.28, 146.95, 147.05, 149.49, 151.50, 161.47. Q-TOF MS/APPI: m/z calcd for C₃₃H₆₃N₂O₃ [M + H]⁺: 525.4051; found: 525.4048.

(E)-1-[3,4-bis( decyloxy) phenyl]oxybenzoyl] diazene (13)

(E)-4-[3,4-bis( decyloxy) phenyl]phenyldiazenyl [phenoxo]octyl]-1-methyl-1 H-imidazol-3-ium bromide (CaNN8lM)

In a two-necked round-bottomed flask with an inlet of gas and equipped with a dropping funnel and a condenser, maintained under constant flow of argon, was transferred 4-decyloxybromobenzene (5.00 g, 16.0 mmol). PdCl₂(PPh₃)₂ (0.112 g, 0.16 mmol) as the catalyst and PPh₃ (0.042 g, 0.16 mmol), followed by dissolution in dry TEA (50 mL). The system was heated, and when it reached 60°C, CuI (0.0152 g, 0.08 mmol) was added, followed by dropwise addition of 2-methyl-3-butyln-2-ol (2.02 g, 24.11 mmol) previously dissolved in dry TEA (20 mL). The reaction
was refluxed for 20 h. The solution was cooled to room temperature, filtered in celite, washed with THF and the solvent was evaporated under reduced pressure. The crude solid was purified over silica gel column chromatography, using hexane/ethyl acetate (95:5) as eluent, affording 4.65 g (92%) of slightly yellow oil, which slowly solidifies. m.p.: 39.8–41.4°C. ¹H NMR (CDCl₃ - 400 MHz) δ ppm: 0.88 (t, J = 6.8 Hz, 3H, -CH₂), 1.24–1.36 (m, 12H, -CH₂-), 1.44 (m, 2H, -CH₂-), 1.61 (s, 6H, -CH₃), 1.77 (m, 2H, -CH₂CH₂O-), 2.05 (s, 1H, -OH), 3.94 (t, J = 6.6 Hz, 2H, -OCH₂-), 6.81 (d, J = 8.8 Hz, 2H, Ar-H), 7.33 (d, J = 8.8 Hz, 2H, Ar-H). ¹³C NMR (CDCl₃ - 100 MHz) δ ppm: 14.35, 22.90, 26.22, 29.40, 29.51, 29.78, 31.78, 32.12, 65.96, 68.27, 82.39, 92.39, 114.63, 133.27, 159.40.

1-decyl-4-ethynylbenzene (15)

To a 100 mL round-bottomed flask were transferred the 4-(4-decyloxyphenyl)-2-methyl-3-buthyn-2-ol (2.94 g, 9.29 mmol) toluene (50 mL) and NaOH (0.37 g, 9.29 mmol). A micro distillation apparatus was adapted and solution was heated via water bath. Reaction end was indicated by TLC and purification was done by silica gel column chromatography using hexane as eluent, affording 2.16 g (90%) of a colourless oil. ¹H NMR (CDCl₃ - 400 MHz) δ ppm: 0.89 (t, J = 6.8 Hz, 3H, -CH₃), 1.25–1.38 (m, 12H, -CH₂-), 1.45 (m, 2H, -CH₂-), 1.78 (m, 2H, -CH₂CH₂O-), 2.99 (s, 1H, =CH), 3.95 (t, J = 6.6 Hz, 2H, -OCH₂-), 6.83 (d, J = 8.8 Hz, 2H, Ar-H), 7.42 (d, J = 8.8 Hz, 2H, Ar-H). ¹³C NMR (CDCl₃ - 100 MHz) δ ppm: 14.37, 22.93, 26.24, 29.40, 29.57, 29.62, 29.80, 32.14, 68.29, 75.90, 84.01, 114.09, 114.67, 133.79, 159.78.

4-iodopyridine (16)

(i) Diazotisation: To a 100 mL round-bottomed flask, 4-aminopyridine (1) (4.00 g, 42.5 mmol) was added, dissolved in HBF₄ (35 mL) and resulting solution was cooled to −10°C with ice/NaCl/acetonite bath. NaNO₂ (1.29 g, 18.7 ml) was then slowly added to the reaction over a period of 45 min. After another 60 min of stirring, the precipitate was filtered in a Büchner funnel, yielding the diazonium salt.

(ii) Sandmeyer reaction: To a saturated solution of KI (11.20 g, 67.40 mmol) in acetonite/water (50 mL, 2:3) was added the diazonium salt. After the addition, reaction was stirred for 10 min, followed by the addition of Na₂S₂O₃ until solution became colourless. The neutralisation was achieved with NaHCO₃ saturated water. The product was extracted with ethyl ether (3 × 150 mL) and the combined organic layer was washed with water (3 × 50 mL). The combined organic phase was then dried with anhydrous Na₂SO₄ and solvent was removed under reduced pressure. The crude solid was purified over silica gel column chromatography, using CHCl₃ as eluent, affording 6.61 g (76%) of an off-white solid. m.p.: 101.1–102.0°C (dec.) (lit. 100–102°C (dec.)) [52]. ¹H NMR (CDCl₃ - 400 MHz) δ ppm: 7.66 (d, J = 5.8 Hz, 2H, Py-H), 8.25 (d, J = 5.8 Hz, 2H, Py-H). ¹³C NMR (CDCl₃ - 400 MHz) δ ppm: 105.63, 133.32, 150.46.

4-(4-decyloxyphenylethynyl)pyridine (17)

To a 125 mL round-bottomed flask, constantly purged with argon, equipped with condenser and dropping funnel were added 4-iodopyridine (16) (0.40 g, 1.94 mmol), PdCl₂(PPh₃)₂ (0.068 g, 0.097 mmol) as the catalyst and PPh₃ (0.025 g, 0.097 mmol), followed by dissolution in a dry TEA/THF system (30 mL, 2:1). The system was heated, and when it reached 60°C, CuI (0.0152 g, 0.080 mmol) was added. At 60°C, dropwise addition of 1-decyl-4-ethynylbenzene (0.50 g, 1.94 mmol) previously dissolved in dry THF (10 mL) occurred. The reaction was refluxed for 3 h. The solution was cooled to room temperature, filtered in celite, washed with THF and solvent was evaporated under reduced pressure. The crude solid was purified over silica gel column chromatography, using CHCl₃ as eluent, affording 4.65 g (92%) of slightly yellow oil, which slowly solidifies. m.p.: 58.1–59.0°C. ¹H NMR (CDCl₃ - 400 MHz) δ ppm: 0.88 (t, J = 6.8 Hz, 3H, -CH₃), 1.25–1.38 (m, 12H, -CH₂-), 1.44 (m, 2H, -CH₂-), 1.78 (m, 2H, -CH₂CH₂O-), 2.99 (s, 1H, =CH), 3.96 (t, J = 5.8 Hz, 2H, -OCH₂-), 6.87 (d, J = 8.6 Hz, 2H, Ar-H), 7.43 (d, J = 6.0 Hz, 2H, Ar-H), 7.46 (d, J = 8.6 Hz, 2H, Ar-H), 8.56 (d, J = 6.0 Hz, 2H, Py-H). ¹³C NMR (CDCl₃ - 400 MHz) δ ppm: 14.35, 22.92, 26.24, 29.38, 29.56, 29.61, 29.79, 29.80, 32.13, 68.36, 85.79, 94.72, 114.03, 114.89, 125.60, 132.13, 133.68, 149.90, 160.20.

1-decyl-4-[4-(decyloxy)phenylethynyl]pyridine-1-ium bromide (CC-10Br)

The following reagents were added to a round-bottomed flask: 4-[(4-decyloxyphenylethynyl)pyridine (17) (0.50 g, 1.49 mmol), 1-bromodecane (0.66 g, 2.98 mmol) and acetonitrile (30 mL) and the mixture was refluxed for 2 days. The solvent was removed under reduced pressure and crude solid was purified using silica gel column chromatography with CHCl₃/methanol (99:1) as eluent, obtaining 0.61 g (83%) of a yellow solid. m.p.: (see Table 1). ¹H NMR (CDCl₃ - 200 MHz) δ ppm: 0.80 (m, 6H, -CH₃), 1.12–1.33 (m, 24H, -CH₂-), 1.40 (m, 4H, -CH₂-), 1.73 (qui, J = 6.6 Hz, 2H, -CH₃CH₂O-), 1.98 (qui, J = 7.2 Hz, 2H, -CH₃CH₂Pir+), 3.93 (t, J = 6.6 Hz, 2H, -OCH₂-), 4.84 (t, J = 7.2 Hz, 2H, Py⁺CH₂-), 6.85 (d, J = 8.2 Hz, 2H, Ar-H), 7.48 (d, J = 8.2 Hz, 2H, Ar-H), 7.92 (d,
$J = 6.0 \text{ Hz}, 2H, \text{Py–H}$, 9.45 (d, $J = 6.0 \text{ Hz}, 2H, \text{Py–H}$).

$^{13}$C NMR (CDCl$_3$ – 400 MHz) δ ppm: 14.08, 22.61, 22.63, 25.92, 26.06, 29.02, 29.09, 29.20, 29.26, 29.30, 29.35, 29.42, 29.49, 31.78, 31.85, 31.88, 61.33, 68.31, 85.14, 106.81, 111.63, 114.99, 128.94, 134.74, 140.89, 144.59, 161.63. Q-TOF MS/ESI: $m/z$ calcd for C$_{33}$H$_{32}$NO [M$^+$]: 476.3887; found: 476.3884. Q-TOF MS/ESI: $m/z$ calcd for Br$: 78.9189; found: 78.9181.

4-[(Decyloxy)phenylethynyl]-1-methylpyridin-1-ium iodide (CC-11)

In a round-bottomed flask were added 4-[(Decyloxy)phenylethynyl]pyridine (17) (0.60 g, 1.79 mmol), iodomethane (1.27 g, 8.95 mmol) and acetonitrile (30 mL), the mixture was heated to 70°C and stirred for 24 h. The solution was cooled to room temperature and the solvent and excess of iodomethane were removed under reduced pressure. Maceration in boiling hexane with drops of methanol yielded 0.83 g (97%) of the pure ionic compound. m.p.: (see Table 1).

$^1$H NMR (CDCl$_3$ – 400 MHz) δ ppm: 0.87 (t, $J = 6.6 \text{ Hz}, 3H, –CH$_3$), 1.21–1.48 (m, 14H, –CH$_2$), 1.78 (m, 2H, –CH$_2$CH$_2$O–), 3.98 (t, $J = 6.6 \text{ Hz}, 2H, –OCH$_2$–), 4.61 (s, 3H, Py’$^+$CH$_3$), 6.90 (d, $J = 8.8 \text{ Hz}, 2H, Ar–H), 7.54 (d, $J = 8.8 \text{ Hz}, 2H, Ar–H), 7.91 (d, $J = 6.6 \text{ Hz}, 2H, Py–H), 9.16 (d, $J = 6.6 \text{ Hz}, 2H, Py–H)$.

$^{13}$C NMR (CDCl$_3$ – 100 MHz) δ ppm: 14.07, 22.72, 25.91, 29.00, 29.26, 29.29, 29.49, 31.83, 49.08, 68.32, 85.13, 107.29, 111.54, 115.01, 128.72, 134.84, 140.06, 144.93, 161.68. Q-TOF MS/ESI: $m/z$ calcd for C$_{23}$H$_{23}$NO [M$^+$]: 350.2478; found: 350.2476. Q-TOF MS/ESI: $m/z$ calcd for I$: 126.9050; found: 126.9033.

4-iodophenol

Prepared as presented in ‘Vogel’s Textbook of Practical Organic Chemistry’, page 930 [53]. m.p.: 90.2–91.8°C (lit. 94°C) [53].

$^1$H NMR (CDCl$_3$ – 400 MHz) δ ppm: 5.25 (s, 1H, Ar–OH), 6.63 (d, $J = 8.5 \text{ Hz}, 2H, Ar–H), 7.51 (d, $J = 8.5 \text{ Hz}, 2H, Ar–H)$.

$^{13}$C NMR (CDCl$_3$ – 100 MHz) δ ppm: 83.08, 118.07, 138.73, 155.46.

1-iodo-4-methoxybenzene (18)

In a 50 mL round-bottomed flask were added 4-iodophenol (5.00 g, 22.7 mmol) and K$_2$CO$_3$ (2.51 g, 18.2 mmol), followed by dissolution in acetone (20 mL). The suspension was stirred for 20 h at 50°C. The system was filtered and solid was washed with CHCl$_3$, solvent was evaporated under reduced pressure. The solid obtained was dissolved in 150 mL of ethyl acetate and organic phase was washed with NaHCO$_3$ saturated aqueous solution and the product was extracted with ethyl ether (100 mL). The organic phase was washed with saturated solution of NaHCO$_3$ (3 × 50 mL), HCl 5% (3 × 50 mL), brine (1 × 50 mL) and distilled water (1 × 50 mL), and was dried with anhydrous Na$_2$SO$_4$. The solvent was evaporated under reduced pressure, affording 5.71 g (96%) of an slowly solidifying oil. m.p.: 33.8–35.6°C (lit. 33–36°C) [55].

$^1$H NMR (CDCl$_3$ – 400 MHz) δ ppm: 2.28 (s, 3H, –COOCH$_3$), 6.86 (d, $J = 8.6 \text{ Hz}, 2H, Ar–H), 7.68 (d, $J = 8.6 \text{ Hz}, 2H, Ar–H)$.

$^{13}$C NMR (CDCl$_3$ – 100 MHz). δ ppm: 21.39, 90.18, 124.06, 138.71, 150.71, 169.33.

4-(Decyloxyphenylethynyl)phenyl acetate (19)

To a 125 mL round-bottomed flask, 4-iodophenol (5.00 g, 22.7 mmol) was dissolved in a mixture of pyridine/acetic anhydride (20 mL, 1:1). The solution was stirred for 18 h and, after that period, acetic anhydride was decomposed with NaHCO$_3$-saturated aqueous solution and the product was extracted with ethyl ether (100 mL). The organic phase was washed with saturated solution of NaHCO$_3$ (3 × 50 mL), HCl 5% (3 × 50 mL), brine (1 × 50 mL) and distilled water (1 × 50 mL), and was dried with anhydrous Na$_2$SO$_4$. The solvent was evaporated under reduced pressure, affording 5.71 g (96%) of an slowly solidifying oil. m.p.: 33.8–35.6°C (lit. 33–36°C) [55].

$^1$H NMR (CDCl$_3$ – 400 MHz) δ ppm: 2.28 (s, 3H, –COOCH$_3$), 6.86 (d, $J = 8.6 \text{ Hz}, 2H, Ar–H), 7.68 (d, $J = 8.6 \text{ Hz}, 2H, Ar–H)$.

$^{13}$C NMR (CDCl$_3$ – 100 MHz). δ ppm: 21.39, 90.18, 124.06, 138.71, 150.71, 169.33.

4-(Decyloxyphenylethynyl)phenyl acetate (20)

To a 125 mL round-bottomed flask, 4-iodophenol (5.00 g, 22.7 mmol) was dissolved in a mixture of pyridine/acetic anhydride (20 mL, 1:1). The solution was stirred for 18 h and, after that period, acetic anhydride was decomposed with NaHCO$_3$-saturated aqueous solution and the product was extracted with ethyl ether (100 mL). The organic phase was washed with saturated solution of NaHCO$_3$ (3 × 50 mL), HCl 5% (3 × 50 mL), brine (1 × 50 mL) and distilled water (1 × 50 mL), and was dried with anhydrous Na$_2$SO$_4$. The solvent was evaporated under reduced pressure, affording 5.71 g (96%) of an slowly solidifying oil. m.p.: 33.8–35.6°C (lit. 33–36°C) [55].

$^1$H NMR (CDCl$_3$ – 400 MHz) δ ppm: 2.28 (s, 3H, –COOCH$_3$), 6.86 (d, $J = 8.6 \text{ Hz}, 2H, Ar–H), 7.68 (d, $J = 8.6 \text{ Hz}, 2H, Ar–H)$.

$^{13}$C NMR (CDCl$_3$ – 100 MHz). δ ppm: 21.39, 90.18, 124.06, 138.71, 150.71, 169.33.
0.194 mmol) as the catalyst and PPh₃ (0.051 g, 0.194 mmol), followed by dissolution in dried TEA (30 mL). The system was heated, and when it reached 70°C, CuI (0.018 g, 0.097 mmol) was added, followed by dropwise addition of 1-decyl-oxy-4-ethynylbenzene (15) (1.00 g, 3.87 mmol) previously dissolved in dried TEA (20 mL). The reaction was refluxed for 7 h. The solution was cooled to room temperature, filtered in celite, washed with THF and solvent was evaporated under reduced pressure. The crude solid was purified over silica gel column chromatography, using hexane/CHCl₃ (1:1) as eluent, followed by maceration in cold methanol, affording 0.93 g (61%) of a slightly yellow solid. m.p.: 92.1–93.4°C. ¹H NMR (CDCl₃ − 400 MHz) δ ppm: 0.88 (t, J = 6.8 Hz, 3H, CH₃), 1.19–1.39 (br, 12H, −CH₂−), 1.45 (m, 2H, −CH₂−), 1.78 (m, 2H, −CH₂CH₂O−), 2.30 (s, 3H, −COOCH₃), 3.96 (t, J = 6.6 Hz, 2H, −CH₂O−), 6.86 (d, J = 8.8 Hz, 2H, Ar−H), 7.07 (d, J = 8.8 Hz, 2H, Ar−H), 7.44 (d, J = 8.8 Hz, 2H, Ar−H). ¹³C NMR (CDCl₃ − 100 MHz) δ ppm: 14.39, 21.39, 22.93, 26.26, 29.43, 29.57, 29.63, 29.80, 29.82, 32.14, 68.31, 87.38, 89.80, 114.75, 115.11, 121.59, 121.87, 132.77, 133.25, 150.38, 159.50, 169.47.

4-(4-decyl-oxyphenylethynyl)phenol

4-((4-(decyl-oxy)phenyl)ethynyl)phenyl acetate (20) (0.75 g, 1.91 mmol) was weighted in a 125 mL round-bottomed flask, dissolved in a methanol/THF system (60 mL, 5:1) and heated to 40°C. KOH (0.21 g, 3.82 mmol) previously dissolved in 10 mL of H₂O was then added to the system. After 1 h, solvent was partially evaporated under reduced pressure and water (100 mL) was added to the system, and pH was adjusted to approximately 3. The product was extracted with ethyl ether (100 mL) and organic phase was subsequently washed with H₂O (2 × 50 mL), followed by drying with anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure and the crude solid was purified using silica gel column chromatography using CH₂Cl₂ as eluent, affording 0.61 g (91%) of a solid. m.p.: 113.3–114.5°C. ¹H NMR (CDCl₃ − 400 MHz) δ ppm: 0.89 (t, J = 6.8 Hz, 3H, CH₃), 1.24–1.37 (br, 12H, −CH₂−), 1.45 (m, 2H, −CH₂−), 1.78 (m, 2H, −CH₂CH₂O−), 3.96 (t, J = 6.6 Hz, 2H, −CH₂O−), 5.11 (s, 1H, Ar−OH), 6.80 (d, J = 8.8 Hz, 2H, Ar−H), 6.86 (d, J = 8.8 Hz, 2H, Ar−H), 7.40 (d, J = 8.8 Hz, 2H, Ar−H). ¹³C NMR (CDCl₃ − 100 MHz) δ ppm: 14.36, 22.92, 26.25, 29.43, 29.56, 29.63, 29.79, 29.81, 32.13, 68.33, 87.94, 88.27, 114.75, 115.59, 115.69, 116.23, 133.09, 133.31, 155.64, 159.23.

1-(8-bromooctoxy)-4-(4-decyl-oxyphenylethynyl) benzene (21)

In a round-bottomed flask equipped with a water condenser were added 4-(4-decyl-oxyphenylethynyl)phenol (0.50 g, 1.43 mmol), 1,8-dibromo-octane (1.17 g, 4.29 mmol) and K₂CO₃ (0.39 g, 2.86 mmol), followed by dissolution in butanone (50 mL). The system was stirred for 20 h at 70°C. The suspension was filtered, solid was washed with CHCl₃ and solvent was evaporated under reduced pressure. The crude solid was purified using silica gel column chromatography with a gradient of hexane/CH₂Cl₂ (from 10:0 to 9:1) as eluent, obtaining 0.67 g (87%) of a white solid. m.p.: Cr − 84°C − SmA − 98°C − Iso. ¹H NMR (CDCl₃ − 400 MHz) δ ppm: 0.89 (t, J = 6.8 Hz, 3H, CH₃), 1.21–1.48 (m, 22H, −CH₂−), 1.78 (m, 4H, −CH₂CH₂O−), 1.86 (m, 2H, −CH₂CH₂Br−), 3.41 (t, J = 6.8 Hz, 2H, −CH₂Br), 3.96 (t, J = 6.5 Hz, 4H, −CH₂O−), 6.85 (d, J = 8.8 Hz, 4H, Ar−H), 7.43 (d, J = 8.8 Hz, 4H, Ar−H). ¹³C NMR (CDCl₃ − 100 MHz) δ ppm: 14.37, 22.93, 26.16, 26.26, 28.32, 28.92, 29.41, 29.39, 29.42, 29.44, 29.56, 29.63, 29.80, 32.14, 33.01, 34.24, 68.18, 68.29, 86.81, 88.15, 88.21, 114.71, 115.68, 115.76, 133.06, 159.13, 159.19.

1-(4-decyl-oxyphenylethynyl)-4-[8-(1-methyl-3imidazoloyl)octyloxy]benzene bromide (CC-8Im)

In a 25 mL round-bottomed flask equipped with a water condenser were added 1-(8-bromooctyl)oxy)-4-(4-decyl-oxyphenylethynyl)benzene (21) (0.50 g, 0.92 mmol) along with 8 mL of 1-methylimidazole. The suspension was irradiated with microwave with initial power of 50 W and maintaining temperature of 90°C for two periods of 5 min. The suspension was then poured in ethyl ether (200 mL), filtered and washed again with ethyl ether. The purification was carried in silica gel column chromatography using CH₂Cl₂/methanol (gradient ranging from 100:0 to 90:10) as eluent, affording 0.52 g (91%) of a white solid. m.p.: (see Table 1). ¹H NMR (CDCl₃ − 400 MHz) δ ppm: 0.88 (t, J = 6.8 Hz, 3H, CH₃), 1.25–1.49 (m, 22H, −CH₂−), 1.80 (m, 4H, −CH₂CH₂O−), 1.93 (m, 2H, Im′CH₂CH₂−), 3.96 (t, J = 6.5 Hz, 4H, −CH₂O−), 4.12 (s, 3H, Im′-CH₃), 4.34 (t, J = 7.4 Hz, 2H, Im′-CH₂−), 6.85 (d, J = 8.8 Hz, 4H, Ar−H), 7.42 (t, J = 1.7 Hz, 1H, Im−H), 7.52 (t, J = 1.7 Hz, 1H, Im−H), 7.43 (d, J = 8.8 Hz, 4H, Ar−H), 10.26 (s, 1H, Im−H). ¹³C NMR (CDCl₃ − 100 MHz) δ ppm: 14.37, 22.90, 26.10, 26.23, 26.33, 28.99, 29.21, 29.24, 29.34, 29.44, 29.42, 29.52, 29.58, 29.75, 29.77, 30.46, 32.14, 37.02, 50.34, 68.20, 68.49, 86.80, 88.17, 114.76, 114.88, 115.69, 115.75, 133.12, 159.10, 159.22. Q-TOF MS/ESI: m/z calcd for C₃₂H₄₁NₙO₂ [M]+: 543.3945; found: 543.3946. Q-TOF MS/ESI: m/z calcd for Br⁻: 78.9189; found: 78.9176.
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