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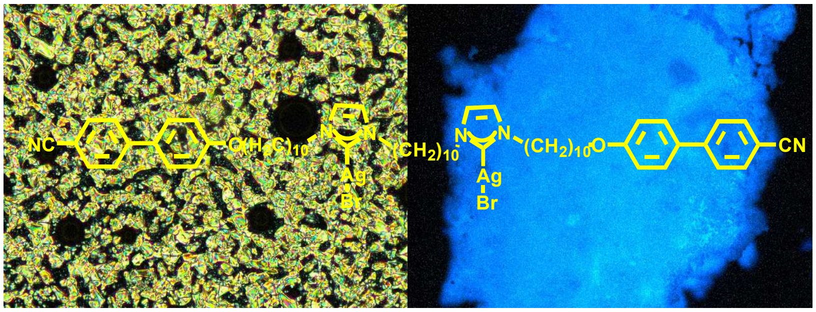
Graphical abstract



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ARTICLE TYPE

# Liquid crystals based on silver carbene complexes derived from dimeric bis (imidazolium) bromide salts

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A series of bis(imidazolium) salts with different mesogenic groups (cyanobiphenyl or cholesteryl) and their silver carbene complexes with $Br^-$ anion has been designed and prepared. The liquid crystalline behaviour of these ionic liquids and their corresponding silver-carbene complexes was investigated by polarised optical microscopy (POM), differential scanning calorimetry (DSC) and powder X-ray diffraction while their thermal stability was studied by thermogravimetric analysis (TGA). The silver complexes are thermally stable on a broad temperature range with accessible transition temperatures close to ambient temperature. The compounds having cholesteryl groups show higher transition temperatures than the compounds possessing cyanobiphenyl mesogenic groups, but their thermal stability is limited by a slight decomposition before reaching the isotropic state. Interestingly, the bis(imidazolium) salt with two cyanobiphenyl gropus at each side shows an enatiotropic nematic phase on a short range, being one of the fewest example of ILC displaying nematic phases.

## Introduction

Imidazolium salts are well-known as ionic liquids (IL) due to their interesting properties such as low volatility, nonflammability and high-ionic conductivity, but also for their liquid crystalline properties (LC), ionic liquid crystals (ILC) that combine in a unique manner the LC and IL properties.[1,2] Imidazolium salts are also attractive as N-heterocyclic carbene (NHC) precursors in organometallic chemistry and homogeneous catalysis.[3] They can form metal complexes with various metals, the resulting complexes having higher thermal stability as well as higher stability towards air and moisture. Numerous studies dealing with LCs based on imidazolium motifs have been reported, including here the flexibly linked bis(imidazolium) salts, the so-called gemini ILC.[4-10] Their liquid crystalline properties range from typical calamitic materials (SmA phase) to discotic materials with long range columnar mesophases, related to mesogenic group employed and the nature of counterion ($Cl^-$, $Br^-$, $NO_3^-$, $BF_4^-$, $PF_6^-$ or $Tf_2N^-$) (Fig. 1). However, reports of liquid crystalline metal-NHC complexes derived from imidazolium cations are few[11] and limited to metals such as Pd,[12] Au and Ag,[13] despite their remarkable thermal stability. While many Ag-NHC with different ways of assembling were reported,[14] only one LC system based on Ag-NHC having long alkyl chains was reported to date by Lin et al.[15] These materials, generally, show a SmA phase which is stable at temperatures above 100°C and, in some cases, they show decomposition during isotropisation. We would like to show that by using appropriate mesogenic groups (cyanobiphenyl or cholesteryl groups) linked to a bis(imidazolium) fragment via flexible alkyl spacers can successfully lead to thermally stable Ag-NHC complexes that show enantiotropic SmA phases at significantly lower temperatures, close to ambient temperatures. The idea of coupling mesogenic groups to various large fragments via a flexible alkyl spacers has been succesfully applied in diferent systems such as fullerene,[16] metallic clusters,[17] lanthanide complexes,[18] etc. Both cyanobiphenyl and cholesteryl groups have been employed for the preparation of imidazolium based ILC.[19-22] In this study, both the type and number of mesogenic groups were varied with the aim of finding the best correlation between these structural features and LC properties of the new silver-NHC materials. Their emission properties were also studied in solution and solid state.

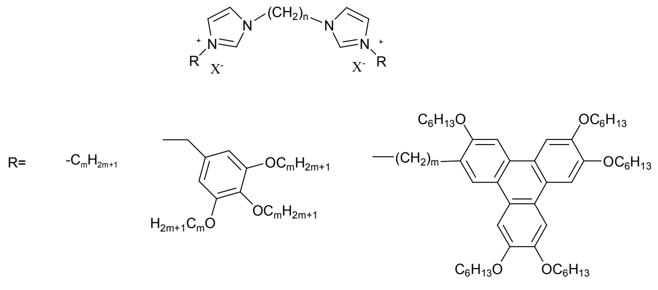

**Fig.1** Structure of dimeric LC bis(imidazole) salts previously reported

## Results and discussion

The new salts were prepared starting from 1,1'-(1,10-decanediyl) bisimidazole, as described by Bara et al.,[7] and different bromide derivatives containing cyanobiphenyl or cholesteryl mesogenic groups (Fig. 2) in acetonitrile under reflux. The products were precipitated with ethyl ether, and purified on silica using

CH$_2$Cl$_2$/MeOH mixture as eluant. These salts proved to be slightly hygroscopic and some amount of water was found both by TG measurements and elemental analysis. As shown in Fig. 2, the new Ag-NHC complexes could be obtained readily in moderate to good yields (35-60%). Their synthesis has been achieved by treatment of the corresponding salts with Ag$_2$O in dichloromethane. Repetead recrystallisations from a mixture of dichloromethane and ethyl ether, accompanied by charcoal decolorisation to remove the silver excess, gave the desired compounds as white or light yellow-brown products. Indeed, the $^1$H-NMR spectroscopy showed no signal higher than 8 ppm, confirming the successful deprotonation of the carbenic protons of bis(imidazolium) **2a-c** salts. In the absence of X-ray structural studies on single-crystal and based on NMR and IR spectroscopy data together with elemental analysis results, these silver complexes can be described by a [Ag$_2$(NHC)Br$_2$] general formula, while the existence of a polymeric structure similar to the one described by Chiu et al.[23] could not be ruled out.

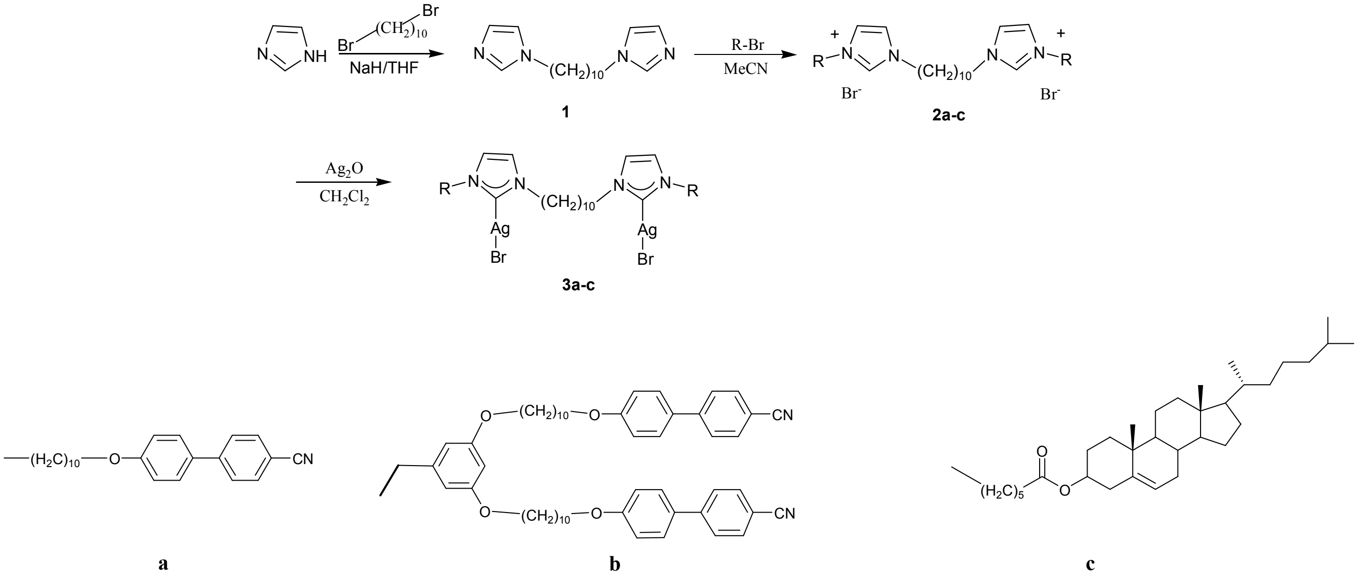

**Fig. 2** Synthesis of dimeric bis(imidazolium) salts and their silver carbene complexes.

The LC phases exhibited by both the bis(imidazolium) salts and their silver complexes were assigned based on the polarised optical microscopy (POM) textures as well as by variable-temperature powder X-ray diffraction and differential scanning calorimetry (DSC) studies. Their transition temperatures and the mesomorphic properties are collected in Table 1. Both **2a** and **2c** salts show a typical fan shape or focal conic texture together with several homeotropic areas that were assigned to a layered SmA phase (ESI, Fig. 1a,c). This phase was found to have a monotropic character for **2a**, and, on further cooling was followed by a crystallization step. The second and the third heating cooling cycles of **2a** perfectly match, with the melting temperature reproducible with the one detected in the first heating-cooling cycle (ESI, Fig. 6). At higher temperatures, compound **2c** show also an oily-streak textures which confirms once again the assignment of a SmA phase (Fig. 3b). Above 135$^0$C, the DSC curve of **2c** shows a series of endothermic and exothermic peaks assigned to a slight decomposition of this product (ESI, Fig. 8). The TG data support this observation and a weight loss of approximately 2.2% was detected in the 135-200$^0$C temperature range (ESI, Fig. 13).

Surprisingly, on cooling from the isotropic liquid, **2b** formed a Schlieren texture accompanied by some marbled texture characteristic to a nematic phase (Fig. 3a). This is quite interesting as it is well known that ILCs tend to show layered phases, mostly SmA, while only few exceptions where a nematic phase was observed for imidazolium based or other type of ILC.[20-24] Further cooling results in regions with a well-developed fan-conical texture indicative of a SmA phase while in other regions this transition to SmA phase is hard to be noticed, probably due to a kinetically-driven transition. The DSC shows only one relatively sharp peak assigned to isotropic to mesophase transition and running with lower scan rates did not result in any separation of the two I-N and N-SmA transitions (ESI, Fig. 7). Generally, the LC properties of the silver complexes, **3a-c**, resembles the ones of the bis(imidazolium) salts, with slightly lower transition temperatures. For instance, **3a** shows an endothermic peak on the first heating run corresponding to transition from the crystalline state to isotropic liquid. On cooling, only one exothermic peak with $T_{onset}$ 49$^0$C was observed and this was assigned to the transition from isotropic to SmA phase (Fig. 4a). In contrast to what was observed for the related bis(imidazolium) salt **2a**, no crystallisation occurred on further cooling and only a glass transition could be detected at 34$^o$C (temperature recorded at half inflexion point). The following heating-cooling cycles are perfectly reproducible and show only one peak corresponding to SmA-I transition and the glass transition in the same interval. For **3b**, the effect of metal center was to reduce the isotropisation temperature about 5$^0$C together with broadening of the mesophase range (about 7$^0$C) (Fig. 4b). Similarly, **3c** shows a much more extended mesophase range when compare to the starting bis(imidazolium) salt **2c**, and, more interesting, a higher thermal stability. In this case the decomposition occurs above 180$^{o}$C, almost 50$^{o}$C greater than the decomposition temperature seen for **2c** (ESI, Fig. 13). Powder X-ray diffraction studies were performed on cooling the samples from the isotropic liquid to the mesophase with the exception of cholesteryl-based compounds, **2c** and **3c**, when the isotropic state could not be reached due to some decomposition at temperatures above 135$^{o}$C. For these two compounds the powder X-ray patterns were recorded on heating, before reaching the decomposition temperatures. All silver complexes show diffraction pattern typically observed for mesophases in the temperature range of liquid crystal phase and frozen, glassy mesophases. The powder X-ray diffraction data for componds **2a-c** and the related silver carbene complexes are shown in Table 2.

**Table 1** Thermal data for bis(imidazolium) salts and their silver carbene complexes

| Compound | Transition | T/$^{o}$C | ΔH(kJ·mol$^{-1}$) |
|---|---|---|---|
| **2a** | Cr-I | 55$^{a}$ | 32.7 |
| | (I-SmA) | 55 | 4.4 |
| | (SmA-Cr) | 34 | 9.2 |
| **2b** | g-SmA | 51 | - |
| | SmA-N | 79$^{b}$ | - |
| | N-I | 81 | 3.9 |
| **2c** | g-SmA | 39 | - |
| | SmA-dec. | 135 | - |
| **3a** | Cr-I | 72$^{a}$ | 44.8 |
| | g-SmA | 36 | - |
| | SmA-I | 54 | 4.9 |
| **3b** | g-SmA | 39 | - |
| | SmA-I | 76 | 10.6 |
| **3c** | g-SmA | 51 | - |
| | SmA-dec. | 180 | - |

$^{a}$ Data taken from the first heating run; $^{b}$Temperature recorded by POM

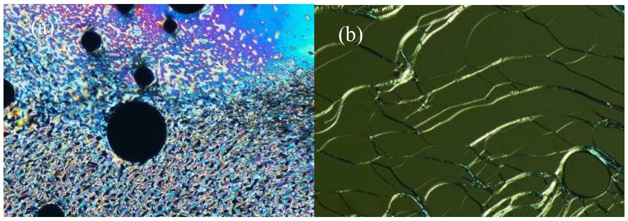

**Fig. 3** Optical texture of **2b** at 79$^{o}$C on cooling (a) and the optical texture of **2c** at 125$^{o}$C on heating (b).

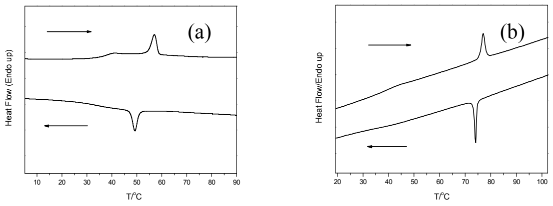

**Fig.4** Second DSC heating-cooling cycle for **3a** (a) and for **3b** (b).

The X-ray diffractogram of **2a** shows three strong reflections in the small angle region in the 1:2:3 ratio that correspond to a periodicity of 40.1Å due to a multilayered smectic phase formed by the imidazole and cyanobiphenyl-containing sublayers alternating with the aliphatic spacer sublayers. For **2b**, the reflections in the low-angle region are not as strong and sharp as for **2a** suggesting a very pronounced disorder of the layered phase. Still, the interlayer distance could be extracted from the d$_{001}$ peak position and it was calculated as 45.1Å. The X-ray patterns of cholesteryl based ILC, **2c** and **3c** (Fig. 5), contain a series of five Bragg diffraction peaks in the low angle region with their ratio 1:2:3:4:5 typical to a layered phase, with layer periodicities of 59.6Å for **2c** and 60.5Å for **3c**.

**Table 2** Powder X-ray diffraction data for bis(imidazolium) salts precursors and their silver carbene complexes

| Compound | T/$^{o}$C | Phase | 2θ | d/Å | Indexation |
|---|---|---|---|---|---|
| **2a** | 44 | SmA | 2.20 | 40.12 | d$_{001}$ |
| | | | 4.38 | 20.16 | d$_{002}$ |
| | | | 6.56 | 13.14 | d$_{003}$ |
| | | | 21.54 | 4.12 | h$_{ch}$ |
| **2b** | 65 | SmA | 1.96 | 45.08 | d$_{001}$ |
| | | | 4.14 | 21.33 | d$_{002}$ |
| | | | 20.58 | 4.31 | h$_{ch}$ |
| **2c** | 81 | SmA | 1.48 | 59.64 | d$_{001}$ |
| | | | 2.98 | 29.62 | d$_{002}$ |
| | | | 4.54 | 19.45 | d$_{003}$ |
| | | | 6.06 | 14.57 | d$_{004}$ |
| | | | 7.52 | 11.75 | d$_{005}$ |
| | | | 16.24 | 5.45 | h$_{ch}$ |
| **3a** | 55 | SmA | 2.00 | 44.14 | d$_{001}$ |
| | | | 5.92 | 14.92 | d$_{003}$ |
| | | | 21.18 | 4.19 | h$_{ch}$ |
| **3b** | 60 | SmA | 1.92 | 45.98 | d$_{001}$ |
| | | | 3.92 | 22.52 | d$_{002}$ |
| | | | 20.50 | 4.33 | h$_{ch}$ |
| **3c** | 80 | SmA | 1.46 | 60.46 | d$_{001}$ |
| | | | 3.02 | 29.23 | d$_{002}$ |
| | | | 4.50 | 19.62 | d$_{003}$ |
| | | | 6.02 | 14.67 | d$_{004}$ |
| | | | 7.54 | 11.72 | d$_{005}$ |
| | | | 16.02 | 5.53 | h$_{ch}$ |

Normally, such interlayer distances resulted from a partial interdigitated molecular organisation to form smectic layers. As it was found for related silver complexes **3a,b**, the interlayer distance is slightly greater than the one corresponding to their bis(imidazolium) precursors and probably this is due to inherent constraints in molecular packing in terms of layer interdigitation.

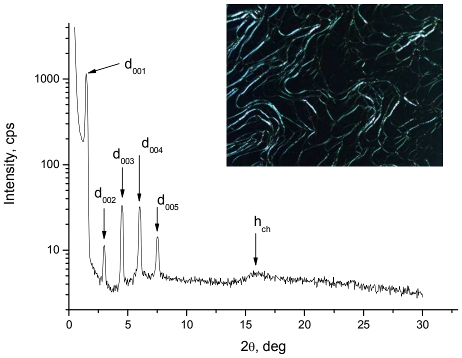

**Fig. 5.** Optical texture of **3c** at 117$^{o}$C on heating (inset) and its X-ray powder diffraction pattern at 117$^{o}$C.

The diffraction patterns of both bis(imidazolium) salts and their silver complexes containing cyanobiphenyl mesogenic groups

(**2a,b** and **3a,b**, respectively) showed a broad peak in the wide-angle region with a spacing of about 4.1Å and correspond to the average lateral separation of the molecule in the LC state. For the remaining compounds, **2c** and **3c** that contain cholesteryl mesogenic groups, this broad peak was located around 5.5Å. The cholesteryl-based compounds have been tested for their capacity to induce chiral nematic phases in common LC materials, 5CB and 5OCB. Indeed in both materials, doping with 1% of **3c** resulted in development of a fingerprint texture in the temperature range of normal existence of the nematic phase for 5-CB and 5-OCB (Fig. 6). Higher concentrations of **3c** produced a phase separation. By using **2c** as dopant, the concentration can be increased up to 3%.

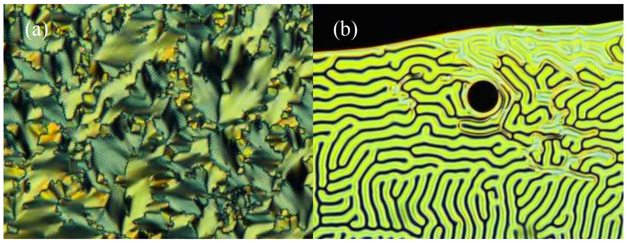

**Fig. 6.** Optical texture of cholesteric phase for **2c** in 5OCB (1%w/w) at 52°C (a) and of **3c** in 5OCB (1% w/w) at 51°C (b).

### Photophysical properties

The luminescent liquid crystals have shown their great potential for use in organic light-emitting diodes (OLEDs). Emissive properties were reported for a series of purely organic liquid crystals[25-27] or metallomesogens and the latter ones were recently reviewed.[28] In this respect, we were interested to investigate the emission properties of the newly prepared silver carbene complexes. Thus, the photophysical properties of bis(imidazolium) salts and their silver complexes have been studied and the results are summarised in Table 3. The electronic absorption spectra of all compounds **2,3a-c**, measured in dichloromethane solutions exhibit one band around 295 nm. As all three bis(imidazolium) precursors, **2a-c**, exhibit emission at room temperature both in solution and solid-state, we were interested to see whether this emission is preserved or enhanced on its complex formation with silver(I) as it was reported previously for other Ag-NHC complexes.[29,30]

**Table 3** Absorption and emission data for bis(imidazolium) salts and their silver complexes in dichloromethane solution and solid state

| Compound | Absorption, $\lambda_{max}$/nm | Emission, $\lambda_{max}$/nm | | $\Phi$/%[a] |
|---|---|---|---|---|
| | | solution | solid[b] | |
| **2a** | 296 | 363 | 433 | 75 |
| **2b** | 295 | 364 | 433 | 63 |
| **2c** | 295 | 363 | 523 | 9 |
| **3a** | 295 | 363 | 451 | 77 |
| **3b** | 296 | 364 | 452 | 60 |
| **3c** | 296 | 364 | 437 | 20 |

[a] Quantum yields were determined with respect to quinine sulphate in 0.1M $H_2SO_4$ at 22°C [b]Recorded in PMMA films

The emission spectra of all three Ag-NHC complexes show an emission structured band at $\lambda_{max}$ around 420-500 nm when the samples are irradiated in the 280-320 nm range both in solid state and as 10% PMMA films. This emission band was found to be red-shifted for **3a,b** and blue-shifted for **3c** when compared to solid-state emission spectra of bis(imidazolium) salts **2a-c** (ESI, Fig. 19). This blue emission has also been visually detected at the optical microscope, both in isotropic and LC phase, when irradiated in the 280-320 nm range (ESI, Fig. 2 and 3). The luminescence properties of all compounds were also studied in dichloromethane solution when only one emission band was observed with its maximum located about 364 nm assigned to an intraligand transition which are blue-shifted by comparison to solid-state emission spectra recorded in either in solid or PMMA films, as it is normally expected. However, the quantum yields of all Ag-NHC compounds recorded in dichloromethane estimated with quinine sulfate ($\Phi$=58% in 0.1M sulfuric acid solution) were found to be very similar to those recorded for ligands, with no significant change, except **3c** where the quantum yield recorded was twice the value recorded for ligand itself, **2c**, but rather low when compared to the cyanobiphenyl-containing derivatives **2,3a,b** supporting the assignment of luminescence attributed to an intraligand rather than a metal-centered process, probably due to the presence of the cyanobiphenyl unit.[31]

## Conclusions

It has been shown that by incorporating the cyanobiphenyl and cholesteryl mesogenic units via a flexible spacer to bis(imidazolium) salts we can prepare silver-NHC complexes that show liquid crystalline materials with smectic phases at significantly lower temperatures, below 100°C, than the examples reported previously. [15] Moreover, a short-range nematic phase was evidenced for a bis(imidazolium) salt that posess four cyanobiphenyl mesogenic groups on each side, which is very uncommon for ionic liquid crystals, in particular for ILC based on imidazolium cations.

We succesfully proved that it is possible to prepare thermally stable silver-NHC complexes with liquid crystalline properties, with decomposition temperatures significantly higher than their bis(imidazolium) precursors. The bis(imidazolium) salts as well as their silver carbene complexes with cyanobiphenyl mesogenic groups are intense blue-emitters, both in solution and solid-state, with appreciable quantum yields in the 60-77% range. No significant change was observed in their emission properties induced by the coordination of silver metal to bis(imidazolium) ligands.

## Experimental

All the chemicals were used as supplied. Cholesteryl 6-bromohexanoate was synthesised as reported elsewhere.[32] C, H, N analyses were carried out with a Perkin Elmer instrument. IR spectra were recorded on a Bruker spectrophotometer using ATR technique. UV-VIS absorption spectra were recorded by using a Jasco V-660 spectrophotometer. $^1H$ and $^{13}C$ NMR spectra were recorded on a Varian Gemini 300 BB spectrometer operating at 300 MHz, using $CDCl_3$ or $CD_2Cl_2$ as solvents. $^1H$ chemical shifts were referenced to the solvent peak position, δ 7.26 or 5.30 ppm. The phase assignments and corresponding transition temperatures for the bis-imidazolium compounds and corresponding silver(I) carbenes were determined by polarizing optical light microscopy (POM) using a Nikon 50iPol microscope equipped with a Linkam

THMS600 hot stage and TMS94 control processor. Temperatures and enthalpies of transition were investigated using differential scanning calorimetry (DSC) with a Diamond DSC Perkin Elmer instrument. The materials were studied at different scanning rates after being encapsulated in aluminium pans. Two or more heating/cooling cycles were performed on each sample with variable scanning rate (2, 5 and 10$^{o}$C/min). Mesophases were assigned by their optical texture and powder X-ray diffraction data. The powder X-ray diffraction measurements were made on a D8 Advance diffractometer (Bruker AXS GmbH, Germany), in parallel beam setting, with monochromatised Cu–K$_{\alpha1}$ radiation (λ=1.5406 Å), scintillation detector, and horizontal sample stage. The measurements were performed in symmetric (θ-θ) geometry in the 2θ range from 1.5$^{o}$ to 10$^{o}$ or 30$^{o}$ in steps of 0.02$^{o}$, with measuring times per step in the 5-40 s range. The temperature control of the samples during measurements was achieved by adapting a home-made heating stage to the sample stage of the diffractometer. Variable temperature emission spectra in solid state were recorded with an OceanOptics QE65PRO spectrometer attached to the microscope and using a Nikon Intensilight excitation source. Fluorescence spectra in solution were recorded on a Jasco FP-6300 spectrofluorometer (operating parameters: band width – 5 nm; data pitch – 0.5 nm; scanning speed – 100 nm/min; spectrum accumulation – 3; path length – 10 mm by using Quartz SUPRASIL cells) in dichloromethane solution. Thermogravimetric analysis was performed on a TA Q50 TGA instrument using alumina crucibles and nitrogen as purging gas. The heating rate employed was 10°C min$^{-1}$ from room temperature (approximately 25°C) to 550$^{o}$C.

**Synthesis of 2a**. 1,1'-(1,10-decanediyl) bisimidazole **1** (1.49 g, 5.47 mmol) was dissolved in acetonitrile. To this solution, 4'-(10-bromodecyloxy) biphenyl-4-carbonitrile (5 g, 12.07 mmol) was added, and the reaction mixture was heated under reflux in nitrogen overnight. After this time, the solvent was removed via rotary evaporation. The residue was purified by column chromatography using silica gel with dichloromethane: methanol (9:1). Yield 80%, white solid. Anal. Calcd. for $C_{62}H_{82}Br_2N_6O_2{\cdot}H_2O$: C% 66.42, H% 7.55, N%7.50. Found: C% 66.78, H% 7.49, N% 7.55. $^1$H NMR (CDCl$_3$, 300 MHz): 10.39 (s, 2H), 7.67 - 7.58 (m, 10H), 7.48 (d, 4H, J=8Hz); 7.42 (s, 2H), 6.94 (d, 4H, J = 8Hz), 4.33 (m, 8H), 3.95 (t, 4H, J = 8Hz), 1.90 (m, 8H), 1.75 (m, 4H), 1.43 - 1.20 (m, 36H). $^{13}$C NMR (CDCl$_3$, 75 MHz): 159.8, 145.3, 136.9, 132.5, 131.2, 128.3, 127.1, 122.6, 121.9, 119.2, 115.1, 109.9, 68.1, 50.0, 49.9, 30.4, 29.9, 29.4, 29.3, 29.2, 29.0, 28.5, 28.1, 26.2, 26.0, 25.6.

IR (ATR, cm$^{-1}$): 2926, 2851, 2223, 1603, 1562, 1523, 1495, 1464, 1291, 1254, 1172, 1035, 822, 724, 633, 564, 531.

**Synthesis of 2b.** 1,1'-(1,10-decanediyl) bisimidazole **1** (70 mg, 0.26 mmol) was dissolved in acetonitrile. To this solution, bromide derivative prepared by a slightly modified procedure as reported elsewhere[33] (0.5 g, 0.57 mmol) was added, and the reaction mixture was heated under reflux in nitrogen overnight. Then, the solvent was removed in vacuum and the residue was purified by column chromatography using silica gel with dichloromethane: methanol (9:1). Yield 76%, white solid. Anal. Calcd. for $C_{122}H_{148}Br_2N_8O_8{\cdot}H_2O$: C% 72.10, H% 7.44, N%5.51. Found: C% 72.05, H 7.56, N. 5.48. $^1$H NMR (CDCl$_3$, 300 MHz): 10.81 (s, 2H), 7.65 (m, 16H), 7.51 (d, 8H, J=8Hz), 7.44 (s, 2H), 7.18 (s, 2H), 6.98 (d, 8H, J=8Hz), 6.54 (s, 4H), 6.42 (s, 2H), 5.46 (s, 4H), 4.33 (m, 4H), 3.99 - 3.89 (m, 16H), 1.94-1.70(m, 20H), 1.50-1.25 (m, 60H). $^{13}$C NMR (CDCl$_3$, 75 MHz): 161.1, 159.9, 145.3, 137.4, 134.9, 132.6, 131.3, 128.4, 127.1, 122.4, 121.6, 119.2, 115.2, 110.1, 107.3, 102.1, 68.5, 68.2, 53.6, 50.1, 29.9, 29.6, 29.5, 29.4, 29.3, 28.4, 28.2, 26.1, 25.7. IR (ATR, cm$^{-1}$): 2980, 2925, 2853, 2223, 1599, 1493, 1465, 1392, 1292, 1248, 1155, 1055, 820, 756, 660, 563, 531.

**Synthesis of 2c**. Cholesteryl 6-bromohexanoate (5 g, 8.88 mmol) was dissolved in 25 mL acetonitrile and 10 mL toluene. 1,1'-(1,10-decanediyl) bisimidazole **1** (1.1g, 4.04 mmol) was added and the reaction mixture was heated under reflux in nitrogen for 24 h. After this period, the solvent phase was removed via rotary evaporation and the residue was purified by column chromatography using silica gel with dichloromethane: methanol (9:1). Yield 57%, white solid. Calcd. for $C_{82}H_{136}Br_2N_4O_4{\cdot}H_2O$: C% 69.37, H% 9.80, N% 3.95. Found: C% 69.12, H 9.75, N. 4.13. $^1$H NMR (CDCl$_3$, 300 MHz):10.49 (s, 2H), 7.60 (t, 2H, J=2Hz), 7.42 (t, 2H, J=2Hz), 5.38 (d, br, 2H), 4.65 - 4.50 (m, 2H), 4.38 (t, 8H, J=7Hz), 2.30 (m, 6H), 1.89-0.85 (m, 102H), 0.65 (s, 6H). $^{13}$C NMR (CDCl$_3$, 75 MHz): 172.8, 139.7, 137.2, 122.7, 122.5, 122.0, 56.8, 56.2, 50.1, 39.6, 35.9, 32.00, 28.3, 28.1, 25.7, 22.9, 22.6, 19.4, 18.8, 11.9. IR (ATR, cm$^{-1}$): 2933, 2855, 1738, 1563, 1457, 1368, 1216, 1120, 528.

**Synthesis of 3a.** A solution of compound **2a** (2.35 g, 2.14 mmol) in freshly distilled dichloromethane and an equivalent amount of Ag$_2$O (0.54g, 2.36 mmol) were stirred at room temperature for 24 h avoiding light exposure. After this period, the suspension was filtered through celite. Then, the solution was treated with charcoal and filtered again. The volume was reduced to about half of the its initial state and ethyl ether was added. The mixture was allowed to stand in the frezeer (-25$^{o}$C). The white crystalline solid formed was isolated by filtration and washed with ethyl ether followed by drying under vacuum. Recrystallisation from dichloromethane/ethyl ether was repetead two times. Yield 64%, white solid. Anal. Calcd. for $C_{62}H_{80}Ag_2Br_2N_6O_2$: C% 56.55, H% 6.12, N% 6.38. $^1$H NMR (CDCl$_3$, 300 MHz): 7.70-7.64 (m, 8H), 7.53 (d, 4H, J=8Hz), 7.00-6.96 (m, 8H), 4.12-4.06 (m, 8H), 4.00 (t, 4H, J=7Hz), 1.81 (m, 12H), 1.48-1.25(m, 36H). $^{13}$C NMR (CDCl$_3$, 75 MHz): 132.7, 128.5, 127.2, 120.8, 115.2, 68.3, 52.0, 31.6, 31.4, 29.5, 29.3, 26.8, 26.7, 26.6, 26.2, 26.1. IR (ATR, cm$^{-1}$): 2927, 2852, 2224, 1632, 1521, 1494, 1465, 1384, 1291, 1251, 1180, 823, 733, 665, 533.

**Synthesis of 3b.** A solution of compound **2b** (0.2 g, 0.17 mmol) in freshly distilled dichloromethane (15 mL) and an equivalent amount of Ag$_2$O (46 mg, 0.20 mmol) were stirred at room temperature for 24 h avoiding light exposure. After this period, the suspension was filtered through celite. Then, the solution was treated with charcoal and filtered again. The volume was reduced to about half of the its initial state and ethyl ether was added. The mixture was allowed to stand in the frezeer (-25$^{o}$C). The white crystalline solid formed was isolated by filtration and washed with ethyl ether followed by drying under vacuum. Recrystallisation from dichloromethane/ethyl ether was repetead two times. Yield 50%, white solid. Anal. Calcd. for $C_{122}H_{146}Ag_2Br_2N_8O_8$: C% 65.77, H% 6.60, N%5.03. Found: C% 65.32, H% 6.43, N% 4.98. $^1$H NMR (CD$_2$Cl$_2$, 300 MHz): 7.67

(m, 16H), 7.55 (d, 8H, J=8Hz), 7.03-6.98(m, 12H), 6.37 (s, 2H), 6.35 (s, 4H), 5.18(s, 4H), 4.08 (t, 4H, J=8Hz), 4.00 (t, 8H, J=8Hz), 3.89 (t, 8H, J=8Hz), 1.81-1.71(m, 20H), 1.47-1.27(m, 60H). $^{13}$C NMR ($CD_2Cl_2$, 75 MHz): 160.8, 159.9, 145.1, 138.3, 132.5, 131.1, 128.3, 126.9, 121.5, 121.0, 119.0, 115.0, 110.0, 106.1, 100.7, 68.2, 30.9, 29.5, 29.4, 29.2, 28.6, 26.00, 25.8. IR (ATR, cm$^{-1}$): 2926, 2853, 2224, 1602, 1522, 1494, 1466, 1392, 1292, 1250, 1177, 1057, 822, 532.

**Synthesis of 3c.** A solution of precursor **3a** (1.1 g, 0.78 mmol) in freshly distilled dichloromethane and an equivalent amount of $Ag_2O$ (0.20 g, 0.86 mmol) were stirred at room temperature for 24 h in dark. Then, the suspension was filtered through celite and the filtrate was treated with charcoal. After filtration, ethyl ether was added, and then it was stored in freezer (-25$^o$C). The solid was filtered and dried in vacuum. The crystallisation step was repetead three times. Calcd. for $C_{82}H_{134}Ag_2Br_2N_4O_4$: C% 60.96, H% 8.36, N% 3.44. Found: C% 60.75, H 8.45, N. 3.63.Yield 35%, yellow-brown solid. $^1$H NMR ($CDCl_3$, 300 MHz): 7.00 (m, 4H), 5.39 (d, br, 2H), 4.65-4.28 (m, 4H), 4.11 (m, 6H), 2.30 (m, 6H), 2.05-0.85 (m, 102H), 0.65 (s, 6H). $^{13}$C NMR ($CDCl_3$, 75 MHz): 172.9, 139.8, 122.8, 121.0, 56.9, 56.3, 52.1, 52.0, 50.2, 39.7, 35.9, 32.1, 32.0, 31.4, 28.4, 28.2, 23.0, 22.7, 19.5, 18.9, 12.0. IR (ATR, cm$^{-1}$): 2934, 2851, 1732, 1639, 1564, 1466, 1377, 1173, 1010, 734.

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## Notes and references

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