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# 2,2'-Biquinolines as test pilots for tuning the colour emission of luminescent mesomorphic silver(I) complexes<sup>†</sup>

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The synthesis and characterization of a series of 2,2'-biquinolines differently substituted in the 4,4'-position and their corresponding silver(1) derivatives obtained through reaction with silver triflate in a 1 : 1 stoichiometric ratio are reported. In order to perform a systematic investigation on the role played by the substituents on the coordination to the silver(1) centre, structural studies through single crystal X-ray diffraction have been performed on two Ag(1) model complexes. Unlike their analogous 2,2'-bipyridine ligands, the biquinolines have been found to behave only as chelated ligands towards the silver(1) ion, irrespective of the substituents. The coordination sphere of the Ag(1) is filled by a solvent molecule and, depending on the presence and nature of the substituents on the organic ligand, by an oxygen atom coming from a coordinated triflate or from a carboxylic group of a symmetrically related molecule, giving rise to neutral or ionic species. For the highest Ag(1) triflate homologues the presence of long and flexible peripheral tails makes it possible to achieve liquid crystalline properties with columnar organization whose high order is due to the large and rigid core. Moreover, the metal coordination induces in all the Ag(1) species interesting emission properties both in solution and condensed states, giving rise to blue or green emitters, depending on the nature of the substituents on the biquinoline units.

### Introduction

Inorganic crystal engineering has been increasingly used over recent years for generating a wide variety of molecular architectures and supramolecular arrangements, properly designed for the development of innovative materials whose properties and functionalities are controlled through the choice of simple and suitable building-blocks.<sup>1-6</sup> The proper control of the selforganizing process is critical for the synthesis of dynamically functional soft materials such as liquid crystals, for which the right combination of specific intermolecular interactions, nanosegregation and molecular shape represents the key point for their synthesis.<sup>7-10</sup> The overall structure is predominantly controlled by the nature of the transition metal ion and the organic ligand chosen, but the network topology and the subsequent physical and optical properties are affected by non covalent interactions, including, in the case of d<sup>10</sup> metal ions, the metallophilic one (aurophilicity).<sup>11</sup> In particular, coordination polymers based on

Ag(I) cations are attracting a great deal of attention due to the high flexibility of the coordination numbers and geometries of the corresponding complexes, above all when based on N-donor pyridyl ligands.<sup>12</sup>

In this context we have been recently involved in the study of 4,4'substituted-2,2'-bipyridines whose great coordination versatility allowed us to tune, in dependence of the counterion and of the substituents used, the electroneutrality, the topology, the supramolecular architectures as well the various properties in a series of silver(I) derivatives.13 Indeed, by selecting proper parameters (coordinating ability of the anion of the silver salt, substituents on the 2,2'-bipyridine ligand, ligand-to-metal stoichiometric ratio) we have been able to drive the supramolecular self-assembly for inducing argentophilic and/or microsegregation responsible for the onset of liquid crystalline properties, in silver(I) derivatives.<sup>14-18</sup> Here we are reporting an extension of our work in which we have investigated the effect of the presence of a larger and more rigid  $\pi$  system introduced on the organic framework (by using 2,2'-biquinolines ligands), exerted on both the supramolecular organization and the thermal behaviour of a series of triflate Ag(I) complexes. For this class of oligopyridines, the presence of two donor atoms and the flexibility of the two quinoline units linked together by a single C–C bond provide the potential for coordinating to metal ions in a variety of modes. The increased aromatic/aliphatic ratio in the biquinoline Ag(I) derivatives should however preserve the proper phase segregation helpful in the formation of liquid-crystalline structures. At the

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same time, fluorescence emission properties of the biquinoline chromophores<sup>19</sup> should expand the applicability of the Ag(I) complexes leading them to be able to tune the photoluminescent properties using phase transitions induced by thermal treatment.

Thus we have designed a series of 2,2'-biquinolines to use as building blocks for the formation of silver(1) complexes through reaction with the moderately coordinating triflate anion in a 1 : 1 ratio (Fig. 1). The influence of the presence/absence and nature of substituents in the p,p' positions with respect to the nitrogen atoms of the ligands on the structure and functional properties of the resulting Ag(1) compounds will be discussed and compared with those of analogous 2,2'-bipyridine-based derivatives.



Fig. 1 Chemical structure, synthesis and related proton numbering scheme of ligands  $L^1-L^4$ .

#### **Results and discussion**

#### Synthesis and structural studies

In order to perform a systematic investigation on the role played by the substituents of the biquinoline ligands in the coordination of the silver(I) centre and in the supramolecular architectures of the metal derivatives, four types of ligands have been used ( $L^{1}$ - $L^4$  in Fig. 1). Starting from the unsubstituted  $L^1$  and the 4,4'bis(methoxycarbonyl)-2,2'-biquinoline  $L^2$  (chosen as model ligands in the construction of small dimensional model complexes), two promesogenic biquinolines  $(L^3-L^4)$  have been designed for promoting nano-segregation and intermolecular interactions in the corresponding triflate silver(I) derivatives. Long aliphatic chains have been introduced through an electron withdrawing link in the 4,4'-bis(hexadecyloxycarbonyl)-2,2'-biquinoline  $L^3$  and a long polycatenar system was grafted on a further aromatic ring through the weakly electron donating methylene group, in the 4,4'-bis[3,4,5-tri(dodecyloxy)benzoyloxymethyl]-2,2'-biquinoline L<sup>4</sup> ligand.

The synthetic strategy used for the synthesis of  $L^2-L^4$  is based on the commercially available 2,2'-biquinoline-4,4'-dicarboxylic acid (I) (Fig. 1). In particular, the Fischer esterification of the precursor I with methanol gave rise directly to ligand  $L^2$ . The preparation of  $L^3$  has been performed through the reaction between I and thionyl chloride, followed by the coupling of the resulting acid chloride with the hexadecyl alcohol. Finally, the reaction between  $L^2$  and the 3,4,5-tridodecyloxy benzoic acid through a DCC– PPY esterification afforded  $L^4$  in a two step procedure:  $L^2$  was reduced to 4,4'-bis(hydroxymethyl)-2,2'-biquinoline with NaBH<sub>4</sub>, and subsequently reacted with 3,4,5-tridodecyloxy benzoic acid through a DCC–PPY esterification.

All the ligands were characterized by elemental analyses, IR, <sup>1</sup>H NMR and UV-vis spectroscopies (Experimental Section) confirming the structure proposed in Fig. 1.

The reaction between the  $L^n$  ligands and silver triflate (AgOTf), performed in a 1:1 ratio for 12 h in chloroform solution (Experimental Section), led to yellowish air stable solids, 1–4, separated in good yields (60–90%).

For all Ag(I) complexes, characterized by elemental analyses, IR, <sup>1</sup>H NMR and UV-vis spectroscopies (Experimental Section), only the 1:1 ligand-to-metal ratio products have been isolated, while the same synthetic pathway followed using a series of analogous 2,2'-bipyridine ligands afforded the formation of products with different stoichiometries (1:1, 2:1 or 3:2 for a 1:1 ligandto-metal ratio) despite the initial proportion used.<sup>13,17-18</sup> Moreover, in the case of the bipyridines reported previously, the presence and the nature of substituents in 4,4' positions was found to drive both their coordination mode (monochelated or bridged) and the participation of the triflate anion to the coordination. in determining the fulfilling of the coordination sphere of the Ag(I) ion. Therefore structural analyses of the model Ag(I) biquinoline derivatives 1 and 2 have been performed in the solid state in order to clarify their effective molecular structure. The main structural feature highlighted by the X-ray single-crystal structures of complexes 1 and 2 is the exclusive chelated coordination mode of the biquinoline to the silver ion, despite their substitution (Fig. 2).



Fig. 2 Perspective view of the asymmetric unit content of 1 (a) and 2 (b) with atomic numbering scheme (ellipsoids at the 40% level).

However, the presence of the carboxylic substituents on the organic ligand  $L^2$  is responsible for a difference in the coordination sphere of the silver ion. In the case of complex 1, one water molecule and the oxygen atom of one triflate anion are coordinated to Ag(1), with the generation of a neutral unit molecule (Fig. 2a). The proximity of the two ligands is such that there is a short distance between the O(2) and O(4) atoms (O ··· O, 2.847(7) Å), which may give rise to an intramolecular hydrogen bond. However, the best calculated positions for the hydrogen atoms bound to the oxygen water molecule do not seem to fulfil the geometrical

parameters characteristic for a significant hydrogen bond [O(4)– $H(4b) \cdots O(2) 2.25 \text{ Å}, O-H \cdots O, 126^{\circ}$ ].

The asymmetric unit of complex **2** is given by a silver cation and a triflate anion non interacting to each other. The silver ion, in a pseudotetra-coordination geometry, is bound to two nitrogen atoms of the chelating  $L^2$  ligand, a water molecule and the oxygen atom belonging to the methoxycarbonyl substituent of a symmetrically related molecule  $[Ag-O(2)^i = 2.699(2) \text{ Å}, i = 2-x, 1-y, -z]$  (Fig. 2b).

In both cases, the crystal packing is characterized by the presence of strong associations between the extended aromatic ligands through  $\pi$ - $\pi$  aromatic stacking interactions and the formation of columns (Fig. 3), characterized by short interplanar distances of about 3.4 Å and indicative of the overlap of the aromatic rings.<sup>20</sup>



**Fig. 3** Crystal packing views of **1** in (a) and **2** in (b) showing the formation of columns with intracolumnar  $\pi$ - $\pi$  aromatic stacking interactions.

Within the columns the strong vicinity of the two molecular units is reinforced by the presence of hydrogen bonds between the coordinated water molecules and the coordinated in 1 and non-coordinated in 2 triflate anions  $[O(4)-H(4A)\cdots O(3) (x, y, z-1), 2.11 \text{ Å}; O\cdots O, 2.858(8) \text{ Å}; O-H\cdots O, 144^{\circ} \text{ for 1; } O(1) H(1w)\cdots O(7) (x+1, y, z-1), 1.89 \text{ Å}; O\cdots O, 2.757(3) \text{ Å}; O H\cdots O, 157^{\circ}, O(1)-H(2w)\cdots O(8) (x, y, z-1), 1.92 \text{ Å}; O\cdots O,$  $2.809(3) \text{ Å}; O-H\cdots O, 171^{\circ} \text{ for 2]}.$ 

In absence of structural studies performed on the highest homologues 3 and 4, the definition of their molecular structure has been based on analogies with complexes 1 and 2. In solution, the success of the coordination of  $L^3$  and  $L^4$  to the Ag(I) ion has been evidenced in the <sup>1</sup>H NMR spectra of **3** and **4** from the upshift of the signals attributable to the H<sup>6,6'</sup> and H<sup>7,7'</sup> protons with respect to the organic precursors. Moreover, in order to define the neutral or ionic nature of complexes 3 and 4 (that is the presence of a coordinated or non coordinated triflate per silver ion) conductivity measurements have been performed in acetone and dichloromethane solutions. In acetone all complexes behave as 1:1 electrolytes (168–180 cm<sup>2</sup>  $\Omega^{-1}$  mol<sup>-1</sup>), thus they undergo a complete ionic dissociation in a polar medium and this can be attributed to the lability of the moderate coordinating triflate group. Therefore we have carried out conductivity measurements in an apolar and non coordinating solvent such as dichloromethane. Even if this solvent usually is not the best for conductivity measurements due to its eventual ion-pairing effects, in these complexes the size of the cation can avoid this limitation. Differently from model compounds 1 and 2 for which the equivalent conductances in dichloromethane have been found to be 6 and 60 cm<sup>2</sup>  $\Omega^{-1}$  mol<sup>-1</sup>

146.8	34.7
166.6	13.3
159.1	15.7
135.0	39.2
72.9	0.73
102.3	34.2
86.2	30.6
	135.0 72.9 102.3 86.2

<sup>*a*</sup> Cr: crystal; Col<sub>L</sub>: lamello-columnar; Col<sub>obp</sub> plastic columnar oblique lattice; I: isotropic liquid. <sup>*b*</sup> Onset peaks, second heating–cooling cycle.

respectively, for **3** and **4** the intermediate values of 25 and 30 cm<sup>2</sup>  $\Omega^{-1}$  mol<sup>-1</sup> are not conclusive to clearly distinguish between neutral or ionic species.<sup>21-22</sup> In the solid state for **1** and **2** a loss of one molecule of water at 95 °C was detected by the TGA analyses (see ESI), while complexes **3** and **4** do not show any water content with any weight loss until 250 °C, where the decomposition starts. Therefore we can hypothesize that the coordination sphere of the Ag(I) ion is completed with the coordination of the triflate ion (such as in complex **1**) and the interaction with an oxygen atom coming from the carboxylic group and/or an anion of a symmetrically related molecule (such as in complex **2**). Both complexes **3** and **4** can be neutral in nature in the solid state but undergo a partial dissociation of the coordinated triflate ion in solution.

#### Thermal properties

The thermal properties of the Ag(I) complexes 3 and 4 (Table 1) based on the biguinolines bearing the longest promesogenic substituents,  $L^3$  and  $L^4$ , respectively, were investigated by using polarised optical microscopy (POM) and differential scanning calorimetry (DSC) with the intention to establish possible analogies with their analogous silver 2,2'-bipyridine triflate derivatives.<sup>17</sup> Although none of the ligands L<sup>n</sup> shows liquid crystalline properties, an interesting thermal behaviour was induced upon complexation. On POM both complexes 3 and 4 show rather fine textures with a limited flowability when subject to stress, whose identification was not unequivocal. In particular, 3 shows, on both heating and cooling cycles (enantiotropically) an uncommon birefringent texture (Fig. 4a) while for the polycatenar complex 4. Maltese crosses appeared after annealing on cooling from the isotropic melt, which developed in the fingerprint texture reported in Fig. 4b.



Fig. 4 Polarized light optical photomicrograph of the textures exhibited by complex 3, at 125 °C on cooling (Plate a); by complex 4 at 71 °C on cooling (Plate b).

The nature of the phases was clarified by powder X-ray diffraction experiments carried out at variable temperatures.

In the small angle range of the X-ray diffraction pattern of **3**, recorded at 155 °C on heating, three diffraction peaks with reciprocal spacings in the ratio 1:2:3 and indexed as (001), (002) and (003) are observed. These three peaks indicate the presence of a very pronounced layered structure, with a repetition distance  $d_{\rm L}$  of 31.9 Å (Fig. 5). Two broad halos are observed in the wide-angle part, centred at 4.3 and 3.4 Å, referred to as  $h_{\rm ch}$  and  $h_0$ , corresponding to the liquid-like order of the molten chains ( $h_{\rm ch}$ ) and the stacking of the molecular cores ( $h_0$ ). These intermolecular interactions are associated with a degree of columnar stacking within the layers, driving towards the assignment of a highly ordered lamello-columnar mesophase, Col<sub>L</sub>.



Fig. 5 X-ray powder diffraction pattern of complex 3 at 155  $^{\circ}$ C on heating; the middle and wide angle regions of the powder pattern in (a) and subtracted background in (b).

The other diffraction peaks, observed in the middle angle region of the spectra, reflect the organization of **3** within each layer. These peaks can be indexed on a two-dimensional monoclinic lattice with parameters a = 9.79 Å, b = 8.96 Å, and an angle  $\gamma$  between the two directions of about 86° (see ESI for indexing and Fig. 6).

For complex 4, the enhancement of the aliphatic periphery grafted around the poly-branched biquinoline ligand  $L^4$  is accompanied by a visible change of thermal behaviour of the corresponding silver(I) derivative. The difference in the molecular anisotropy and the volume of the two silver(I) compounds changes their phase stability, lowering by 60 °C the clearing temperature of 4 with respect to 3. Moreover, the high viscosity and the texture developed on POM, the relatively high enthalpy transition value at the isotropization, could be indicative of the formation of a high ordered columnar phase.23 Since columnar ordered phases prove to be the closest relation to crystalline structures, they are often considered and defined as "soft crystals" instead of liquidcrystalline systems. Moreover, when the sample can be sheared easily, as in this case, unlike other three-dimensionally ordered phases, the definition of plastic columnar phase  $(Col_p)$  is also applied.24



Fig. 6 Proposed packing diagram for the  $Col_L$  phase of 3 showing (a) the layered repetition of columns and (b) the monoclinic columnar organization within the layers.

To investigate the structure of the phase in complex 4, the X-ray powder pattern was recorded at 30 °C on cooling (Fig. 7). A set of several peaks was observed in the small and middle angle region of the powder pattern and successfully indexed as a two-dimensional oblique lattice with lattice parameters a = 42.1Å, b = 35.8 Å and  $\gamma = 112.3^{\circ}$  (see ESI). This is in agreement with the formation of a columnar structure with the resulting columns packed into an oblique lattice (Fig. 8). The plastic nature of this columnar phase is evident from the wide angle region of the X-ray powder pattern (see ESI).<sup>25,26</sup> Indeed, a relatively intense and sharp reflection at 4.4 Å (indexed as the (001) reflection) under the broad halo  $h_{ch}$  reveals additional intracolumnar periodicity and indicates a degree of three-dimensional order of the molecules within the columns. Furthermore, the stack of the molecules is reinforced by  $\pi$ - $\pi$  stacking interactions, as confirmed by the broad  $h_0$  reflection centred at 3.6 Å.



**Fig. 7** X-ray powder diffraction pattern of complex **4** at 30 °C on cooling; the middle and wide angle regions of the powder pattern in the inset.



**Fig. 8** Proposed packing diagram for the Col<sub>obp</sub>. phase of **4** showing the repetition of ordered columns packed into an oblique lattice.

Moreover, on cooling from the isotropic liquid, complex 4 does not crystallize but solidifies into a glassy state retaining the structure of the mesophase. All of these findings point towards the assignment of a plastic columnar phase with an oblique symmetry,  $Col_{obp}$ .

Comparing the behaviour of **3** with that reported for the analogous silver 2,2'-bipyridine triflate derivative,<sup>17</sup> it seems that the change of the oligopyridine, although causing a drastic change in the coordination mode and the global molecular shape, does not affect the lamello-columnar nature of the mesophases formed. However, in the case of the polycatenar substituted biquinoline derivative **4**, the increased number of terminal chains drives to a pure highly ordered columnar arrangement.

#### Photophysical properties

The photophysical behaviour of the chromophore 2,2'biquinolines and the corresponding Ag(I) derivatives has been investigated both in solution and in their condensed states (ESI).

In the room temperature absorption spectra of  $L^{1}-L^{4}$  recorded in dichloromethane solution three groups of bands are detected (see ESI), all originating from  $\pi$ - $\pi^{*}$  transitions on the aromatic rings of the 2,2'-biquinoline: an intense band (maximum spanning in the 250–290 nm range, depending on the compound considered) originating from an excitation on the pyridyl ring of the quinoline ligand; a series of medium-intensity bands (in the 290–350 nm range) due to vibronic components of an intraligand chargetransfer (ILCT) from the pyridyl to the phenyl ring of the quinoline unit, and a weak band (in the 350–390 nm range) attributed to an ILCT from the pyridyl ring of a quinoline moiety towards the phenyl ring of another quinoline.<sup>26-27</sup>

By comparing the absorption spectra of the ligands, it can be noted that the spectrum of the unsubstituted biquinoline  $L^1$  is substantially the same as that of  $L^4$ , both being characterized by a vibrational structure which indicates an accentuated molecular rigidity in solution; this feature is absent in the spectra of  $L^2$  and  $L^3$ . In  $L^1$  and  $L^4$  a great stabilization derives from an extended electronic delocalization on both the quinoline rings, which forces the molecule into a rigid and planar *trans* conformation. In contrast, the introduction of electron-withdrawing substituents, such as esteric groups, directly connected to the phenyl rings of  $L^2$  and  $L^3$  (the length of the alkoxy chains is irrelevant to the electronic properties) reduces the delocalization and allows a degree of torsion around the  $\sigma$ -bond connecting the quinolinic moieties. Therefore the spectra of  $L^2$  and  $L^3$  lose the vibrational

Table 2 Photophysical data of ligands and complexes

complex	$Em, \lambda_{max}/nm$				
	$CH_2Cl_2$ solution ( $\Phi$ )	powder sample	mesophase		
	410 (0.010)	415			
$L^2$	448 (0.035)	460			
$L^3$	452 (0.010)	460			
$L^4$	425 (0.015)	430			
1	478 (0.006)	519			
2	525(0.040)	556			
3	525(0.016)	560	560		
4	453 (0.022)	490	460		

structure and show a weakening of the low-energy absorption band due to the quinoline co-planarity defeat that reduces the oscillator strength of the ILCT between the two quinoline moieties.<sup>28</sup>

The complexation forces all the molecules into a rigid and planar *cis* conformation, regardless of the stabilization effect induced by the electronic delocalization; so the dichloromethane solution absorption spectra of the silver(1) complexes **1–4** are all vibrationally structured. The d<sup>10</sup> metal co-ordination does not influence the electronic transitions already active in the ligands, and the spectral features of all complexes are unvaried with respect to those of the corresponding ligands, showing a bathochromic shift only.

As regards the luminescence, all the ligands in dichloromethane solution and in the solid state emit, irrespective of the wavelength excitation (Table 2). Both the unsubstituted and polycatenar ligands,  $L^1$  and  $L^4$  emit in the violet region while the reduced rigidity achieved with the presence of the esteric substituents in  $L^2$  and  $L^3$  shifts the emission maxima towards the blue region.

The luminescence of complexes **1–4**, which is due to the metalperturbed ILCT state de-excitation, is strongly red-shifted in solution (about 100 nm) with respect to that of the corresponding biquinoline precursors (Table 2). Therefore complexes **1** and **4** emit in the blue region while **2** and **3** behave as green emitters.

Solid samples of 1-4 complexes show a remarkable luminescence, having the same origin of the compounds in solution, but the maxima are red-shifted with respect to the corresponding spectra recorded in solution. This behaviour is attributed to the intermolecular interactions existing in the condensed phase, allowing a certain degree of electronic delocalization. Comparing the spectral shift amount within complexes 1-4, it is possible to note that in 1 the shift of the emission maximum from 478 nm in solution to 519 nm in the solid state is more relevant with respect to the other complexes, raising, in terms of energy, the value of 1653 cm<sup>-1</sup>. Therefore this compound changes from blue to green emitter by passing from the solution to the solid state, while the other complexes in solid retain a green (2 and 3) or a blue emission (4) like in solution. This effect is directly related to the enhancement of vibrational motions in the solid state of complexes 2-4, due to the presence of mobile substituents on the biquinoline ligand, when compared to complex 1. Since in solution vibrational motions are relevant, in the solid phase of complex 1 the vibrational losses are very low in absence of mobile substituents.

Moreover, the luminescent properties of complexes 3 and 4 are kept in their mesophases. Indeed, maxima centred at 560 and

460 nm, respectively, are detected. These values are very similar to those of their solid samples, proving the small differences existing between the intermolecular interactions responsible for the two aggregation states.

#### Conclusions

The use of 2,2'-biquinoline ligands in the coordination of silver(1) ion has proven to be a good strategy for the generation of a series of mononuclear silver(I) complexes starting from silver triflate in a 1:1 metal-to-ligand stoichiometric ratio. Unlike their analogous bipyridine-based Ag(I) complexes, the enlarged aromatic portion of the 2,2'-biquinolines pushes them to coordinate in an exclusive chelating mode to the silver(I) ion.<sup>17</sup> The presence of appropriate terminal tail lengths on the biquinolines allows the existence in the corresponding Ag(I) derivatives, 3 and 4, of intermolecular interactions and micro-segregation able to induce liquid crystalline behaviour. However, while in the case of 3 the lamello-columnar nature of the mesophase is retained, changing the oligopyridine from 2,2'-bipyridine to 2,2'biquinoline ligand,<sup>17</sup> for the polycatenar derivative 4, the increased aromatic flat portion of the core induces the formation of a highly ordered (plastic) columnar arrangement with an oblique symmetry.

Moreover, the biquinoline chromophores as nitrogen ligands promote in their silver(I) derivatives, luminescence properties completely absent in the similar bipyridine-based Ag(I) complexes. Therefore complexes 1-4 emit in the blue or green region depending on both the aggregation state and the substituents on the biquinoline fragment. In particular, the introduction of substituents on the biquinoline ligands plays an important role in the modulation of the emission colours. The induction of a certain degree of molecular motion is able to reduce the shift of the emission maximum on going from the solution to the solid state in the case of complexes 2-4. Therefore, only the unsubstituted complex 1 changes from green to blue emitter by passing from the solution to the solid state, while the other complexes retain a green (2 and 3) or a blue emission (4) like in solution. Moreover, complexes 3 and 4 preserve the luminescence properties also in their mesophases. Due to this invariance of the photophysical properties on moving towards a soft type of aggregation state, it is possible to tune the emission colours of these systems simply by introducing changes at a molecular level, such as the presence of different substituents on the aromatic core.

This type of self-organized anisotropic soft materials has a great potential in a wide variety of fields of advanced technology preserving the same emission properties shown at room temperature.

#### **Experimental section**

#### Materials and measurements

Silver triflate (AgOTf) and 2,2'-biquinoline-4,4'-dicarboxylic acid were purchased from Aldrich and used as received.  $L^2$  was obtained through a small modification of a procedure reported in the literature.<sup>29</sup> For the synthesis of the bicatenar 2,2'-biquinoline ligand ( $L^3$ ) and the hexacatenar 2,2'-biquinoline ligand ( $L^4$ ), a syn-

thetic route reported previously in the literature was followed.<sup>30,31</sup> <sup>1</sup>H NMR spectra were acquired on a Bruker Avance DRX-300 spectrometer in CDCl<sub>3</sub> solution, with TMS as internal standard. Infrared spectra were recorded with a Spectrum One FT-IR Perkin-Elmer spectrometer. Elemental analyses were performed with a Perkin-Elmer 2400 microanalyzer by the Microanalytical Laboratory at the University of Calabria. Conductivity measurements were performed in dichloromethane and acetone, with an InoLab Cond Level 1-720 conductometer equipped with a LR 325/001 immersion cell. The transition temperatures and enthalpies were measured on a Perkin-Elmer Pyris1 Differential Scanning Calorimeter with a heating and cooling rate of 10 °C min<sup>-1</sup>. The apparatus was calibrated with indium. Three heating/cooling cycles were performed on each sample. Thermogravimetry (TGA) measurements were performed on a Perkin-Elmer TGA6 Thermogravimetric Analyser, with a heating rate of 10 °C min<sup>-1</sup>. Spectrofluorimetric grade solvents were used for the photophysical investigations in solution, at room temperature. A Perkin-Elmer Lambda 900 spectrophotometer was employed to obtain the absorption spectra. Steady-state emission spectra were recorded on a HORIBA Jobin-Yvon Fluorolog-3 FL3-211 spectrometer equipped with a 450 W xenon arc lamp, doublegrating excitation and single-grating emission monochromators (2.1 nm mm<sup>-1</sup> dispersion; 1200 grooves/mm), and a Hamamatsu R928 photomultiplier tube. Emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard correction curves. Emission quantum yields were determined using the optically dilute method<sup>32</sup> on aerated solutions of which absorbance at excitation wavelengths was < 0.1; Ru(bipy)<sub>3</sub>Cl<sub>2</sub> (bipy = 2,2'bipyridine) in water ( $\Phi = 0.028$ )<sup>33</sup> or 9,10-diphenylanthracene in cyclohexane ( $\Phi = 0.96$ )<sup>34</sup> were used as standards. Luminescence spectra from powder samples and from mesophase have been obtained placing the powder between two quartz plates, in such a position that the luminescence could be measured in reflection mode, in front-face arrangement to reduce the scattered light. To reach the mesophase, the two quartz plates were heated in the sample compartment of the spectrofluorimeter by means of a customized hot stage realized by CaLCTec s.r.l. (Rende, Italy).

The experimental uncertainty on the molar extinction coefficients is 10%, while that on the emission quantum yields is 10%. The examined compounds are fairly stable in solution, as demonstrated by the constancy of their absorption spectra over a week.

#### Powder X-ray diffraction

The powder X-ray diffraction patterns of **3** and **4** at variable temperature were obtained using a Bruker AXS General Area Detector Diffraction System (D8 Discover with GADDS) with Cu-K $\alpha$  radiation ( $\lambda = 1.54056$  Å). Measurements were performed by placing samples in Lindemann capillary tubes with an inner diameter of 0.05 mm. The highly sensitive area detector was placed at a distance of 20 cm from the sample (20 detector placed at 14°) and equipped with a CalCTec (Italy) heating stage. The samples were heated at a rate of 5.0 °C min<sup>-1</sup> to the appropriate temperature.

	1	2
Formula	$C_{19}H_{14}AgF_{3}N_{2}O_{4}S$	$C_{23}H_{18}AgF_{3}N_{2}O_{8}S$
Mr	531.25	647.32
Crystal size/mm	$0.22 \times 0.15 \times 0.12$	$0.35 \times 0.22 \times 0.18$
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\overline{1}$
a/Å	13.5936(7)	7.2305(16)
b/Å	20.5452(12)	12.765(3)
c/Å	7.1974(4)	13.307(3)
α (°)	90	83.416(10)
$\beta(\circ)$	98.058(3)	81.940(10)
γ (°)	90	86.948(10)
$V/Å^3$	1990.27(19)	1207.2(4)
Ζ	4	2
$\rho$ calcd [g cm <sup>-3</sup> ]	1.773	1.781
$\mu/\mathrm{cm}^{-1}$	1.174	0.998
θ range [°]	1.51-27.98	1.55-28.28
data collected	19 398	23 305
unique data, R <sub>int</sub>	4774, 0.0279	5904, 0.0263
obs. data $[I > 2\sigma(I)]$	2931	4602
no. parameters	271	343
$R_1$ [obs. data]	0.0519	0.0331
$wR_2$ [all data]	0.1653	0.0867
GOF	1.061	1.027

 Table 3
 Details of data collection and structure refinements for complexes 1 and 2

#### X-ray crystallography

X-ray data for 1 and 2 were collected at room temperature on a Bruker-Nonius X8 Apex CCD area detector equipped with graphite monochromator and Mo-K $\alpha$  radiation ( $\lambda = 0.71073$ Å). Data were processed through the SAINT<sup>35</sup> reduction and SADABS<sup>36</sup> absorption software. The structures were solved by standard Patterson methods through the SHELXTL-NT<sup>37</sup> structure determination package and refined by full-matrix leastsquares based on  $F^2$ . In general, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as idealized atoms riding on the respective carbon atoms with C-H bond lengths appropriate to the carbon atom hybridization. Hydrogen atoms of the co-ordinated water molecules have been included in calculated positions in 1, and detected in the difference Fourier map and then their position included in the refinement in 2. In both cases restraining bond distances and angles have been used.

Details of data and structure refinements are given in Table 3. CCDC 805766 (1) and 805767 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data\_request/cif.

#### Synthesis of 4,4'-bis(methoxycarbonyl)-2,2'-biquinoline, ligand L<sup>2</sup>

 $L^2$  was obtained through a Fischer esterification with methanol, in presence of  $H_2SO_4$ , starting from the commercially available 2,2'biquinoline-4,4'-dicarboxylic acid. In particular, the dicarboxylic acid (2.0 g, 5.808 mmol) was suspended in 300 mL MeOH and 40 mL of  $H_2SO_4$  was added slowly. The reaction mixture was then heated to reflux and stirred until the total solubilisation of the suspension. Then the yellowish solution was cooled to room temperature, the solvent evaporated and slowly a saturated solution of NaOH was added until pH 9. The white precipitate formed was filtered out, washed with water and MeOH and dried. Yield 95%. M. p. 288 °C. Anal. Calcd. for  $C_{22}H_{16}N_2O_4$  (372.37): C, 70.96; H, 4.33; N, 7.52; Found: C, 70.83; H, 4.35; N, 7.45. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  9.33 (2H, s, *H3*); 8.82 (2H, d, <sup>3</sup>*J* = 8.4 Hz, *H8*); 8.43 (2H, d, <sup>3</sup>*J* = 8.4 Hz, *H5*); 7.83 (2H, dt, <sup>3</sup>*J* = 7.7 Hz, <sup>4</sup>*J* = 1.5 Hz, *H7*); 7.70 (2H, dt, <sup>3</sup>*J* = 7.8 Hz, <sup>4</sup>*J* = 1.4 Hz, *H6*); 4.13 (s, 6H, COOC*H*<sub>3</sub>); IR (KBr):  $v_{C=0}$  1733 cm<sup>-1</sup>.

## Synthesis of 4,4'-bis(hexadecyloxycarbonyl)-2,2'-biquinoline, ligand L<sup>3</sup>

A mixture of the commercially available 2,2'-biguinoline-4,4'dicarboxylic acid (1.0 g, 2.904 mmol) and thionyl chloride (70 mL) was refluxed under nitrogen atmosphere until a clear vellow solution was obtained. The excess of thionyl chloride was then removed and the residue dried under vacuum for 2 h. The acid chloride was suspended in toluene (50 mL) and treated with a small excess of 1-hexadecanol (1.690 g, 6.970 mmol). The mixture was heated at reflux until a weakly pink solution was obtained (18 h). Then the temperature was cooled to room temperature, the solvent evaporated, chloroform was added and the mixture was washed with saturated sodium hydrogen carbonate solution and three times with water. The pure product was obtained after recrystallisation from CHCl<sub>3</sub>-MeOH (2.07 g, yield 90%). M. p. 101 °C. Anal. Calcd. for C<sub>52</sub>H<sub>76</sub>N<sub>2</sub>O<sub>4</sub> (793.17): C, 78.74; H, 9.66; N, 3.53; Found: C, 78.51; H, 9.29; N, 3.85. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  9.31 (2H, s, *H3*); 8.79 (2H, d, <sup>3</sup>*J* = 8.6 Hz, *H8*); 8.32 (2H, d, <sup>3</sup>*J* = 8.3 Hz, *H5*); 7.82 (2H, t, <sup>3</sup>*J* = 7.7 Hz, *H7*); 7.69 (2H, t,  ${}^{3}J = 7.7$  Hz, H6); 4.53 (t, 4H,  ${}^{3}J = 6.7$  Hz, OCH<sub>2</sub>); 1.92 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>); 1.37 (overlapped peaks, 52H); 0.87 (t, 6H,  ${}^{3}J = 6.8$ Hz, CH<sub>3</sub>); IR (KBr):  $v_{C=0}$  1724 cm<sup>-1</sup>.

#### Synthesis of 4,4'-bis[3,4,5-tri(dodecyloxy)benzoyloxymethyl)]-2,2'-biquinoline, ligand L<sup>4</sup>

To a suspension of ligand L<sup>2</sup> (1.7 g, 4.5 mmol) in ethanol (130 mL) was added slowly an excess of NaBH<sub>4</sub> (4.14 g, 0.110 mol) and the reaction mixture was refluxed for 5 h. Subsequently, to the yellow solution obtained saturated NH<sub>4</sub>Cl solution (90 mL) was added slowly. The white precipitate formed was filtered out, washed with water, dried and used without further purifications in the next step (4,4'-bis(hydroxymethyl)-2,2'-biquinoline, yield 83%). 3,4,5-Tridodecyloxy benzoic acid (1.0 g, 1.481 mmol), 4,4'bis(hydroxymethyl)-2,2'-biquinoline (0.213 g, 0.673 mmol) and 4pyrrolidinopyridine (Ppy, 0.100 g, 0.673 mmol) were dissolved in the minimum volume of dry CH<sub>2</sub>Cl<sub>2</sub> under nitrogen atmosphere. The temperature was then cooled down to 0 °C. After 20 min, N,N'-dicyclohexylcarbodiimide (0.306 g, 1.481 mmol) dissolved in the minimum volume of dry CH<sub>2</sub>Cl<sub>2</sub> was added dropwise. The reaction mixture was stirred at room temperature and under N<sub>2</sub> for five days. The white precipitate formed was then eliminated by filtration and the pure ligand was isolated after recrystallisation from CHCl<sub>3</sub>-MeOH (0.990 g, yield 41%). M. p. 115 °C. Anal. Calcd. for C<sub>106</sub>H<sub>168</sub>N<sub>2</sub>O<sub>10</sub> (1630.48): C, 78.08; H, 10.39; N, 1.72; Found: C, 78.59; H, 10.40; N, 2.01. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  9.03 (2H, s, *H3*); 8.25 (2H, d, <sup>3</sup>J = 8.4 Hz, *H8*); 8.11 (2H, d,  ${}^{3}J = 8.2$  Hz, H5); 7.79 (2H, t,  ${}^{3}J = 7.6$  Hz, H7); 7.65 (2H, t,  ${}^{3}J =$ 7.6 Hz, H6); 7.38 (s, 4H, b-H2); 5.90 (s, 4H, CH<sub>2</sub>OOC); 4.03 (m, 12H, OCH<sub>2</sub>); 1.77 (m, 12H, OCH<sub>2</sub>CH<sub>2</sub>); 1.35 (overlapped peaks, 108H); 0.87 (t, 18H,  ${}^{3}J = 6.3$  Hz, CH<sub>3</sub>); IR (KBr):  $v_{C=0}$  1714 cm<sup>-1</sup>.

#### General procedure for the synthesis of silver(I) complexes 1-4

The synthesis of the complexes 1-4 was carried out starting from the appropriate  $L^n$  ligand in a 1:1 ratio with silver triflate. The reaction mixture in chloroform was heated to reflux and stirred for 12 h, under nitrogen atmosphere and in vessel protected by light.

#### Synthesis of complex 1

The yellowish precipitate formed after 12 h of reaction is filtered out and washed with ethylic ether (yield 68%). M. p. 257 °C. Anal. Calcd. for C<sub>19</sub>H<sub>14</sub>AgF<sub>3</sub>N<sub>2</sub>O<sub>4</sub>S (531.25): C, 42.96; H, 2.66; N, 5.27; Found: C, 42.90; H, 2.65; N, 5.26. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.87 (2H, d,  ${}^{3}J$  = 8.6 Hz, H3); 8.34 (2H, d,  ${}^{3}J$  = 8.6 Hz, H8); 8.25  $(2H, d, {}^{3}J = 8.6 \text{ Hz}, H4); 7.90 (2H, d, {}^{3}J = 7.9 \text{ Hz}, H5); 7.77 (2H, d, H2); 7.77 (2H, H2); 7$ t,  ${}^{3}J = 7.3$  Hz, H7); 7.59 (2H, t,  ${}^{3}J = 7.3$  Hz, H6); IR (KBr):  $v_{\text{orf}}$ 1381 cm<sup>-1</sup>;  $\Lambda$  (C<sub>M</sub> = 2.6 × 10<sup>-4</sup> mol L<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>) = 6 cm<sup>2</sup>  $\Omega$ <sup>-1</sup> mol<sup>-1</sup>;  $\Lambda$  (C<sub>M</sub> = 5.7 × 10<sup>-5</sup> mol L<sup>-1</sup>, acetone) = 186 cm<sup>2</sup>  $\Omega$ <sup>-1</sup> mol<sup>-1</sup>.

#### Synthesis of complex 2

The yellowish precipitate formed after 12 h of reaction is filtered out and washed with ethylic ether. The pure product was recovered from the solution by evaporating the solvent (yield 86%). M. p. 264 °C. Anal. Calcd. for C23H18AgF3N2O8S (647.33): C, 42.67; H, 2.80; N, 4.33; Found: C, 42.35; H, 2.70; N, 4.24. <sup>1</sup>H NMR (300 MHz,  $(CD_3)_2CO$ :  $\delta$  9.34 (2H, s, H3); 8.77 (2H, d,  ${}^{3}J$  = 8.8 Hz, H8); 8.37 (2H, d, <sup>3</sup>*J* = 8.4 Hz, *H*5); 7.80 (2H, t, <sup>3</sup>*J* = 7.8 Hz, *H*7); 7.71 (2H, t,  ${}^{3}J$  = 7.0 Hz, H6); 4.19 (6H, s, COOCH<sub>3</sub>); IR (KBr):  $v_{C=0}$ 1726 cm<sup>-1</sup>,  $v_{\text{OTf}}$  1225 cm<sup>-1</sup>;  $\Lambda$  (C<sub>M</sub> = 3.7 × 10<sup>-5</sup> mol L<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>) = 61 cm<sup>2</sup>  $\Omega^{-1}$  mol<sup>-1</sup>;  $\Lambda$  (C<sub>M</sub> = 1.4 × 10<sup>-4</sup> mol L<sup>-1</sup>, acetone) = 168 cm<sup>2</sup>  $\Omega^{-1}$  mol<sup>-1</sup>.

#### Synthesis of complex 3

After 12 h of reaction, the reaction mixture was filtered through celite and the pure product was obtained after recrystallisation from CHCl<sub>3</sub>-Et<sub>2</sub>O as a yellowish solid (yield 88%). Anal. Calcd. for C<sub>53</sub>H<sub>76</sub>AgF<sub>3</sub>N<sub>2</sub>O<sub>7</sub>S (1050.11): C, 60.62; H, 7.29; N, 2.66; Found: C, 60.55; H, 7.11; N, 2.44. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 9.31 (2H, s, H3); 8.79 (2H, dd,  ${}^{3}J = 8.6$  Hz,  ${}^{4}J = 1.4$  Hz, H8); 8.32 (2H, d,  ${}^{3}J = 8.3$  Hz, H5); 7.82 (2H, t,  ${}^{3}J = 7.7$  Hz, H7); 7.69 (2H, t,  ${}^{3}J = 7.7$  Hz, H6); 4.53 (4H, t,  ${}^{3}J = 6.7$  Hz, OCH<sub>2</sub>); 1.92 (4H, m,  $OCH_2CH_2$ ); 1.35 (52H, overlapped peaks); 0.87 (6H, t,  ${}^{3}J = 6.8$ Hz, CH<sub>3</sub>); IR (KBr):  $v_{C=0}$  1723 cm<sup>-1</sup>,  $v_{OTf}$  1358 cm<sup>-1</sup>;  $\Lambda$  (C<sub>M</sub> = 3.0  $\times 10^{-5} \text{ mol } L^{-1}, CH_2Cl_2) = 25 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}; \Lambda (C_M = 5.7 \times 10^{-5} \text{ mol}^{-1})$  $L^{-1}$ , acetone) = 180 cm<sup>2</sup>  $\Omega^{-1}$  mol<sup>-1</sup>.

#### Synthesis of complex 4

After 12 h of reaction, the reaction mixture was filtered through celite and the pure product was obtained after recrystallisation from CHCl<sub>3</sub>/hexane as a white solid (yield 93%). Anal. Calcd. for C<sub>107</sub>H<sub>168</sub>AgF<sub>3</sub>N<sub>2</sub>O<sub>13</sub>S (1887.41): C, 68.09; H, 8.97; N, 1.48; Found: C, 68.28; H, 9.19; N, 1.61. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.95 (2H, s, *H3*); 8.24 (2H, d, <sup>3</sup>*J* = 8.1 Hz, *H8*); 8.07 (2H, m, *H5*); 7.60 (2H, m, H6, H7); 7.35 (2H, s, b-H2); 6.02 (4H, s, CH<sub>2</sub>OOC); 4.01 (4H, m, OCH<sub>2</sub>); 1.72 (12H, m, OCH<sub>2</sub>CH<sub>2</sub>); 1.35 (108H, overlapped peaks); 0.87 (18H, m, CH<sub>3</sub>). IR (KBr): v<sub>C=0</sub> 1717

 $cm^{-1}$ ,  $v_{OTf}$  1220  $cm^{-1}$ ;  $\Lambda$  ( $C_M = 1.6 \times 10^{-5} \text{ mol } L^{-1}$ ,  $CH_2Cl_2$ ) = 30  $cm^2$ 

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 $\Omega^{-1}$  mol<sup>-1</sup>.

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