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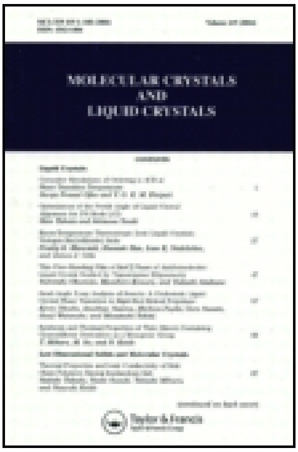

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Soft Luminescent Materials Based on Ag(I) Coordination Complexes

Elisabeta I. Szerb [a], Daniela Pucci [a], Alessandra Crispini [a] & Massimo La Deda [a]

[a] Centro di Eccellenza CEMIF.CAL-LASCAMM, CR-INSTM Unità della Calabria, Dipartimento di Chimica e Tecnologie Chimiche - CTC, Università della , Calabria , Italy

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Soft Luminescent Materials Based on Ag(I) Coordination Complexes

ELISABETA I. SZERB,* DANIELA PUCCI, ALESSANDRA CRISPINI, AND MASSIMO LA DEDA

Centro di Eccellenza CEMIF.CAL-LASCAMM, CR-INSTM Unità della
Calabria, Dipartimento di Chimica e Tecnologie Chimiche – CTC,
Università della Calabria, Italy

The synthesis and characterization of a new liquid-crystalline columnar 2,2′-bipyridine silver complex containing the 2,2′-bipyridine and benzoate as ancillary ligand, both functionalized with long alkyl chains was performed, along with a full photophysical investigation both in solution and in different condensed states. Furthermore, in order to get more insights about their solid-state architectures, structural studies have been performed on a model complex. The new complexes are luminescence in solution, but on passing to the condensed states, this luminescence is quenched or red-shifted, as a function of different "soft" or "hard" organizations inducted by varying the temperature.

Supplemental materials are available for this article. Go to the publisher's online edition of Molecular Crystals and Liquid Crystals to view the free supplemental resources: crystallographic data and table for ***Bz1****. CCDC reference number 922531.*

Keywords Coordination chemistry; Luminescence; Metallomesogens

Introduction

Coordination complexes based on Ag(I) cations and N-donor pyridyl ligands have proved to give rise to a wide variety of molecular architectures and supramolecular arrangements, controlled simply by changing the nature of the molecular building blocks or reaction parameters (solvent, reagents ratio, and temperature) [1].

In this context, we are interested in the application of the inorganic chemistry engineering in the field of liquid crystalline Ag(I) materials, to generate soft architectures with tunable photophysical properties. It is worthy to mention that mesomorphic Ag(I) derivatives are promising multifunctional materials for applications in electro-optical devices, and therefore, the understanding of the relationship between structure and properties is essential for a fine tuning of the photophysical properties of the final material [2]. Structural studies conducted on model molecules demonstrate how important the nature of the different molecular parts is in the generation of specific intermolecular interactions in the three-dimensional space [3]. In the area of liquid-crystalline Ag(I) materials, we reported several works regarding supramolecular assemblies constructed by using as building blocks

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*Address correspondence to Elisabeta I. Szerb, Centro di Eccellenza CEMIF.CAL-LASCAMM, CR-INSTM Unità della Calabria, Dipartimento di Dipartimento di Chimica e Tecnologie Chimiche – CTC, Università della Calabria, Via P. Bucci Cubo 14C Italy. Fax: +39 0984 492066. E-mail: e.szerb@unical.it differently functionalized oligopyridines and counterions with variable coordination capacities [4–8]. The change in the supramolecular structure and the inherent tuning of the photophysical properties both in solution and in condensed state of the final materials was followed by changing the nature of the N,N'-donor ligand (from 2,2′-bipyridines to 2,2′-biquinolines differently functionalized with two or six long alkyl chains), the nature of counterions (perchlorate – ClO_4^-, trifluoromethanesulphonate – OTF^-, and dodecylsulphate – DOS) and reaction conditions. Consequently, lamello-columnar and columnar mesophases of different symmetries were obtained and, in some cases, it was possible to investigate the photophysical properties of the Ag(I) complexes within the soft or condensed phases.

In particular, we followed two strategies. First, the coordination of the Ag(I) centre with two chelating 2,2′-bipyridine-based ligands differently functionalized with several long alkyl chains yielded disc-shaped ionic complexes of general formula $[(bpy\text{-}R)_2Ag]X$ presented in Chart 1. These complexes furthermore self-assembly into columnar mesophases, whose symmetry depended on the type of the counterion used. In particular, the more voluminous DOS counterion forced the arrangement into a more constrained rectangular geometry [4]. The introduction of a chiral centre in the molecular structure, yielded room temperature mesomorphism and blue emission in the liquid-crystalline state of the final complexes [6].

Furthermore, the lowering of the stoichiometric ratio between the Ag(I) metal centre and the N,N'-donor ligand to 1:1, resulted in a self-assembly of the complexes in different supramolecular architectures, principally tuned by the coordinating ability of the counterion (Chart 2) [7,8].

In particular, using the moderately coordinating *OTf* counterion, a chiral supramolecular polymeric network arrangement in the solid state [7] or blue emission in the mesophase [8], were observed (Chart 2).

These stimulating results prompted us to investigate functional benzoates as more versatile building blocks in the construction of supramolecular Ag(I) assemblies. Indeed,

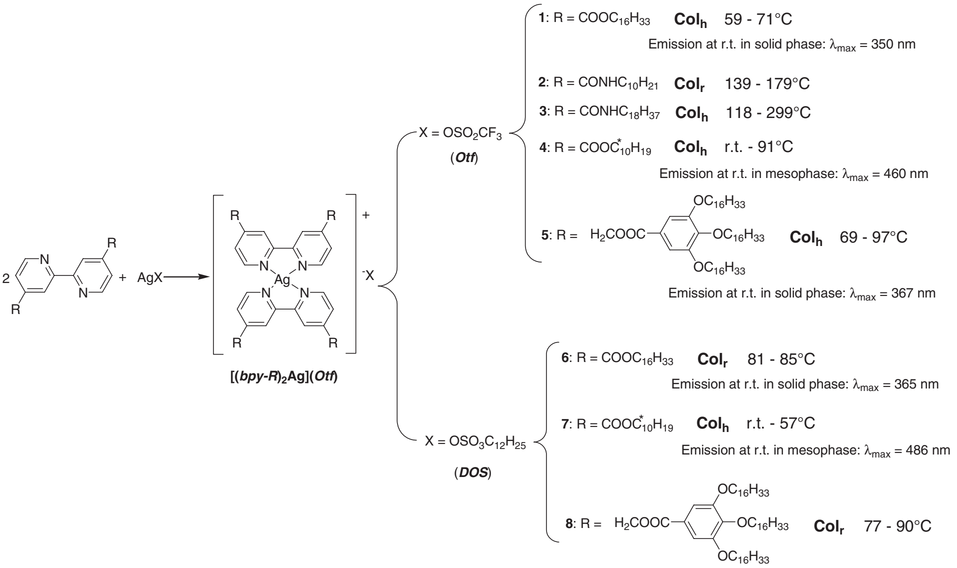


Chart 1. Chemical structure, mesomorphism, and photophysical properties in solid and mesophase for ionic Ag(I) complexes containing two bipyridine-based ligands [4–6].

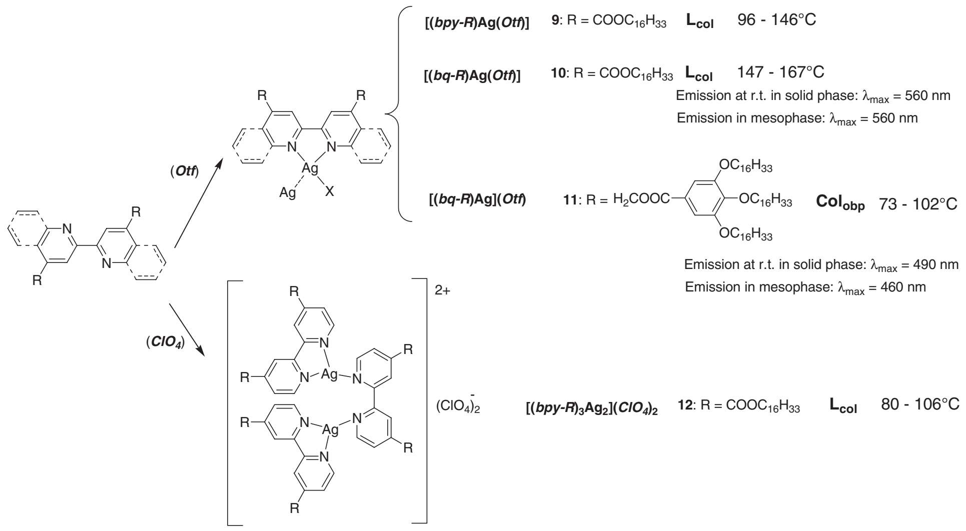


Chart 2. Chemical structure, mesomorphism, and photophysical properties in solid and mesophase for Ag(I) complexes with 1:1 or 3:2 ligand to metal ratio [7,8].

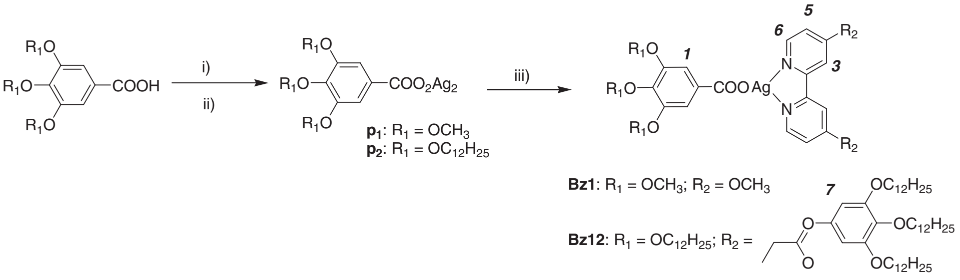
benzoates may act as counterions [9,10] as well as monodentate [11] or bidentate [12] ancillary ligands, yielding thus very different stereochemical arrangements. Furthermore, the easiness of functionalization with long alkyl chains into the benzoate ions, affords a simple way to increase the aliphatic part in the molecular structure of the resulting complexes [13].

Therefore, as an extension of our work regarding soft materials based on Ag(I) complexes, herein, we report on the synthesis and characterization of a new liquid-crystalline complex, Bz12, containing a 2,2′-bipyridine functionalized with several long alkyl chains as main ligand and the 3,4,5-dodecyloxybenzoate as complementary ligand. As main ligand we used the promesogenic ligand 4,4′-bis[3,4,5-(tris-dodecyloxy)benzoyloxymethyl]-2,2′-bipyridine, (*bpy-H*$_{12}$) that resulted from our previous studies less versatile in the coordination towards Ag(I) ion, yielding always tetracoordinated ionic complexes [4]. In these complexes, the columnar mesophase symmetries observed, depended on the type of the counterion used. The introduction of a noninnocent ligand like the functionalized benzoate, can induce the formation of a different coordination environment around the Ag(I) metal centre, therefore, changing drastically the molecular structure and influence the photophysical properties of the system. Furthermore, in order to clarify the structure of the final complexes, we prepared a model complex, Bz1, using as main ligand the 4,4′-dimethoxy-2,2′-bipyridine (*bpy-C*$_1$) and 3,4,5-methyloxybenzoate as complementary ligand, on which a structural study has been performed through single-crystal X-ray diffraction.

Results and Discussion

Synthesis and Characterization

The synthesis of the new Ag(I) complexes is presented in Scheme 1. In particular, dimeric [13] Ag(I) alkyloxybenzoates p_1 and p_2, were obtained starting from the appropriate benzoic acid derivatives [14] adapting a synthetically procedure reported in the literature [15]. The



Scheme 1. Synthesis and proton numbering of complexes Bz1 and Bz12: (i)NaOH, EtOH/H_2O, r.t., 2 hours; (ii) $AgNO_3$, r.t., 2 hours; and (iii) *bpy-C₁* or *bpy-H₁₂*, $CHCl_3$, r.t., 16 hours.

corresponding complexes Bz1 and Bz12 were obtained by stirring for 16 hours at room temperature (r.t.) in a vessel protected by light, a solution in chloroform of the two precursors [16], respectively the Ag(I) benzoates (*p_1* or *p_2*) and the proper bipyridinic ligands (*bpy-C_1* or *bpy-H_{12}*) (Scheme 1).

The structural characterization and purity of the new derivatives reported herein (Bz1 and Bz12) were investigated by IR and ^1H NMR spectroscopies and elemental analysis, the data being presented in the experimental section. Furthermore, the neutral character in CH_2Cl_2 solution was assessed by conductivity measurements for both complexes experimental section (ESI) [8,17].

The coordination environment of the Ag(I) derivatives Bz1 and Bz12 in solution, was examined through proton ^1H NMR measurements. Both spectra showed similar chemical shifts for the aromatic protons, respectively, protons 3, 5, and 6 from the 2,2′-bipyridine ligand and proton 9 from benzoate. In particular, proton 3 is upfield shifted, whereas all other aromatic protons shift at higher ppm with respect to the precursors (2,2′-bipyridine ligand and silver benzoates, respectively). This suggests a similar structure of the two complexes at least in solution.

IR spectra may give information in order to distinguish between the possible coordination type of the benzoate ions, looking at the C–O stretching frequencies [11a]. In particular, an increase of the antisymmetrical C–O stretching or a decrease of the symmetrical one may be an indication of the monodentate coordination mode. This is evident for both complexes, Bz1 and Bz12 when compared with their precursors, *p1* and *p2*, respectively, where, as reported before, the benzoate has a bidentate coordination mode (see Experimental Part). Indeed, the C–O antisymmetrical stretching frequency increases for both complexes, (of 21.6 cm^{-1} and 67.9 cm^{-1} for Bz1 and Bz12, respectively), whereas the symmetrical stretching remains more or less around the same frequency of the precursor.

Thermogravimetric analysis (TGA) measurements conducted on both complexes showed a relatively good thermal stability, with decomposition occurring above 200°C, and the absence of coordination solvents in the pristine solids, confirmed also by elemental analysis.

In the case of the model complex Bz1, single crystals suitable for X-ray diffraction analysis were grown in CH_2Cl_2 solution. As it is shown in Fig. 1(a), the Ag(I) ion, three coordinated by the N,N-chelated bipyridine and the monodentated O-bonded 3,4,5-methyloxybenzoate ligand (intramolecular distance Ag–O(4) of 2.892(5) Å), exhibits a distorted T-shaped coordination geometry, with the N(1)-Ag-O(3) angle of 154.1(1)° and the Ag-N(1) bond distances 0.12 Å shorter than the corresponding Ag-N(2) value. The

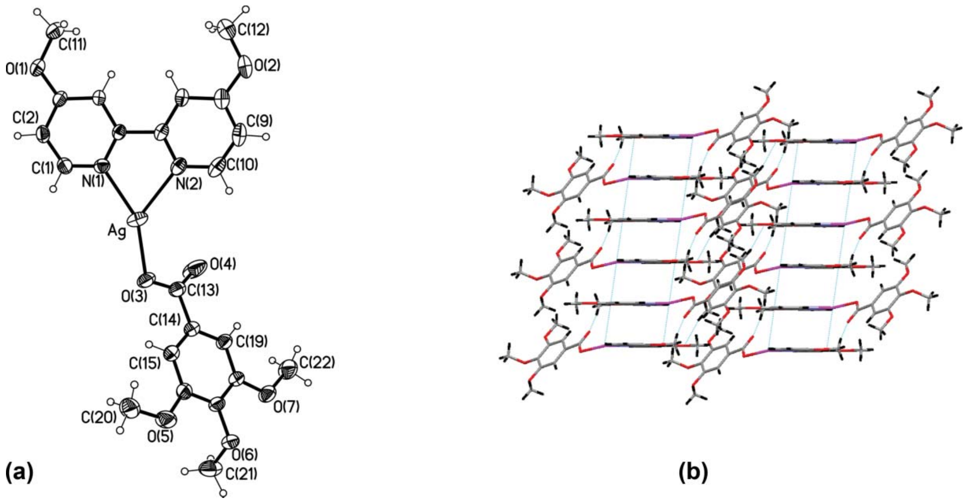


Figure 1. Perspective view of complex Bz1 with atomic numbering scheme (ellipsoids at the 40% level) (a) and its packing diagram illustrating the formation of columns along the *a* direction between association of dimers of molecules (b).

two pyridyl rings of the bipyridine ligand are found highly coplanar with the torsion angle C(4)-C(5)-C(6)-C(7) of 1.6(1)°.

The crystal packing of Bz1 is built up through the repetition of dimers of molecules organized in a head-to-tail arrangement to each other along the *a* direction (Fig. 1(b)). Within the dimer and between dimers strong ring-to-metal interactions exist, as proved by the distances, between the centroid of the pyridine ring of one molecule and the Ag(I) ion lying above, of 3.5 and 3.7 Å, and the angle between the centroid – Ag vector with the normal to the aromatic plane of 22 and 28°, respectively.

Mesomorphism

The thermal behaviour of complex Bz12 was investigated by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and small-angle X-ray diffraction on powder samples (PXRD).

Complex Bz12 exhibits an enantiotropic liquid-crystalline phase from almost r.t. (36.4°C) to 59.2°C (Table 1). On POM, a bright blue fan-shaped texture with homeotropic

Table 1. Optical and thermal data for complex Bz12

	Transition[a]	T/°C	$\Delta H/kJ\cdot mol^{-1}$
First Cycle	C–Col_h	36.4	18.9
	Col_h–I	59.2	73.3
	I–Col_h	59.1	4.6
Second Cycle	Col_h–I	60.0	5.5
	I–Col_h	59.3	5.4

[a] C: crystal; Col_h: columnar hexagonal mesophase, I: isotropic liquid.

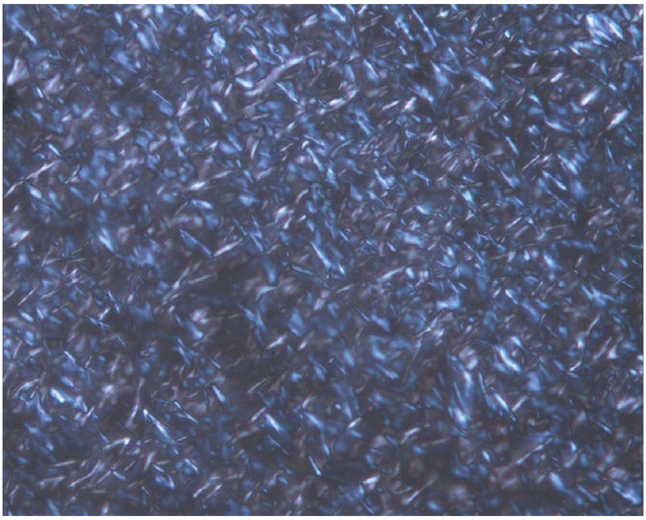


Figure 2. POM micrograph of the texture developed by complex Bz12 on cooling at 50°C.

zones was observed on cooling (Fig. 2) suggesting a columnar hexagonal mesophase. The DSC scan contains only in the first heating cycle two transitions, corresponding to C–$\mathrm{Col_h}$ transition and Colh–I, respectively. On cooling and further heating-cooling cycles only the second transition is observed.

An overview of the transition temperatures and the corresponding detectable enthalpies is given in Table 1.

The distinct identification of the mesophase was made by PXRD. The X-ray pattern of complex Bz12 (Fig. 3(a)) recorded on cooling at 50°C consists, in the small angle region, of four reflections in the ratio $1 : \sqrt{3} : \sqrt{4} : \sqrt{7}$ characteristic of a two-dimensional lattice of a hexagonal columnar phase, corresponding to the indexation $(hk) = (10), (11), (20)$, and (21), with cell parameter $a = 37.8$ Å. The fluid-like nature of the phase is confirmed by the diffuse and broad-scattering halo h centered at 4.4 Å at wide angles of the X-ray pattern (Fig. 3).

On cooling at r.t., the hexagonal columnar arrangement is kept in a kind of glassy state and broad reflections appear in the wide-angle region of the PXRD pattern indicating the formation of relatively strong intracolumnar interactions (Fig. 3(b)).

Photophysical Behavior

The photophysical properties of Bz1 and Bz12 were firstly collected in diluted dichloromethane solutions, obtaining absorption, emission, and excitation spectra. As shown in Fig. 4, the two spectra set have nearly the same shape. In particular, the absorption bands of Bz1 (consisting of a maximum at 258 nm followed by a shoulder at 290 nm) are blue-shifted with respect to the corresponding bands of Bz12 (270 and 300 nm, respectively). Both samples show an emission maximum centered at 350 nm. These features are ascribed to $\pi \rightarrow \pi^*$ transitions localized on the bipyridine rings, slightly perturbed by the silver coordination.

Interesting results are obtained when both compounds are examined as neat samples, placing the microcrystalline powders between two quartz windows and recording their

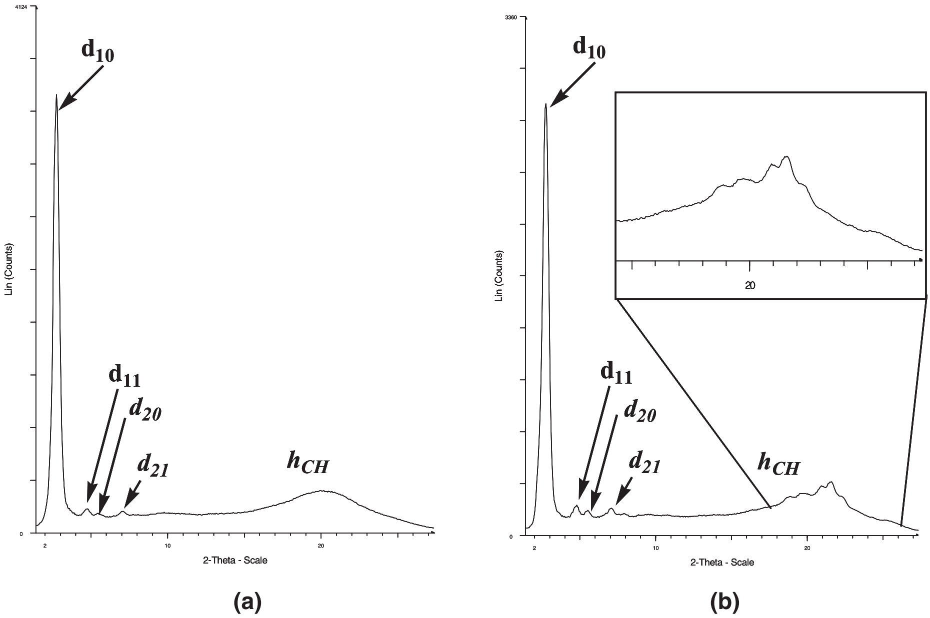


Figure 3. PXRD pattern of Col$_h$ phase of complex Bz12 (a) at 50°C on first cooling; (b) at r.t. after the first heating-cooling cycle.

photophysical properties varying the temperature. During these heating-cooling cycles, Bz1 and Bz12 yielded different results.

Compound Bz1 is not luminescent at room temperature as pristine powder solid, and this behavior is retained until the melting point (172°C). At this end, the isotropic sample

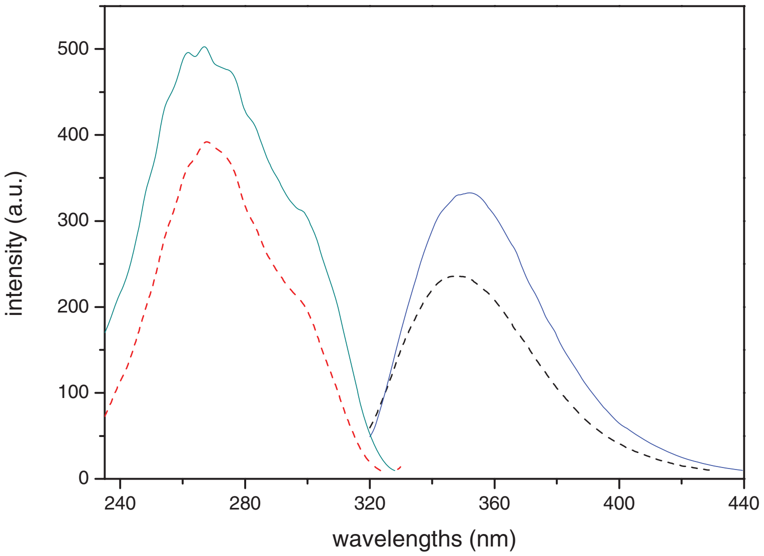


Figure 4. Excitation (on the left) and emission (on the right) spectra of Bz1 (dotted line) and Bz12 (continuous line) in dichloromethane solution.

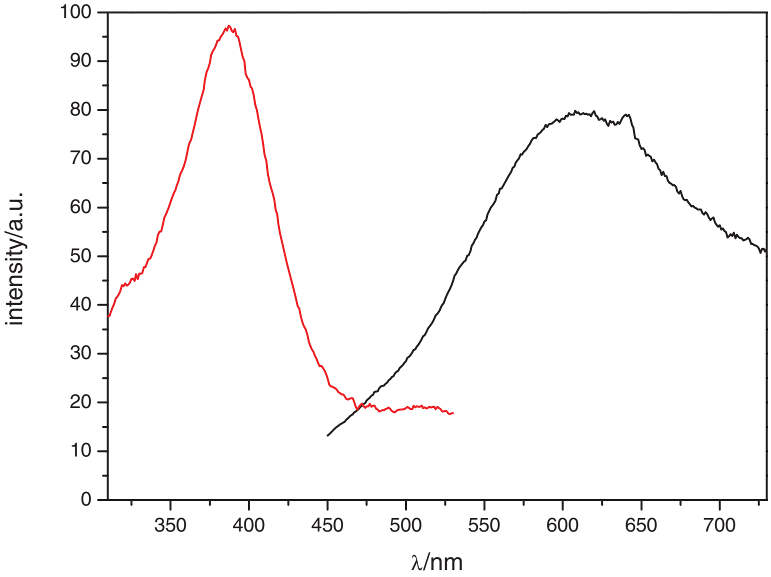


Figure 5. Excitation (on the left) and emission (on the right) spectra of Bz1 obtained in the condensed state at r.t. after one heating-cooling cycle.

shows an emission with a maximum centered at 615 nm, which is kept on cooling the sample until room temperature. Figure 5 shows the cooled sample emission and excitation spectra, whose shape are independent on further temperature changes. The excitation spectrum shows a band at 390 nm, absent in the spectrum recorded in solution.

By comparing these results with those obtained in solution, it can be concluded that in the pristine solid state, complex Bz1 experiences intermolecular interactions able to quench the luminescence showed in a diluted solution, where the photophysical properties of the single molecule are evidenced. Most likely, in the isotropic state the contacts between the chromophores are weakened, allowing for a recovery of the luminescence experienced as a single molecule in the solution. The persistence of the molecular interactions in the isotropic state accounts for the red-shifting of the excitation and emission bands with respect to the solution spectra.

Compound Bz12 shows a more complex behavior following the thermal course. Indeed, like compound Bz1, the microcrystalline solid state sample of Bz12 does not emit at room temperature and becomes luminescent after the melting point (59.2°C) is reached, showing a maximum at 580 nm (the corresponding excitation spectrum shows a peak at 370 nm and a shoulder at 420 nm; Fig. 6). During the cooling cycle, the emission is retained, and the intensity increases until 40°C. At room temperature no luminescence is detected.

It is reasonably to suppose that, like compound Bz1, strong intermolecular interactions existing in the solid state of complex Bz12, quench the molecular luminescence. In the isotropic state, the intermolecular contacts between the chromophores are reasonable weakened, therefore again the luminescence is partially recovered. On cooling from the isotropic state, a highly disordered liquid crystalline phase is formed (between 80°C and 40°C), where the absence of intermolecular interactions within the columns is proved by the absence of indicative reflections in the wide angle region of the PXRD pattern (Fig. 3(a)).

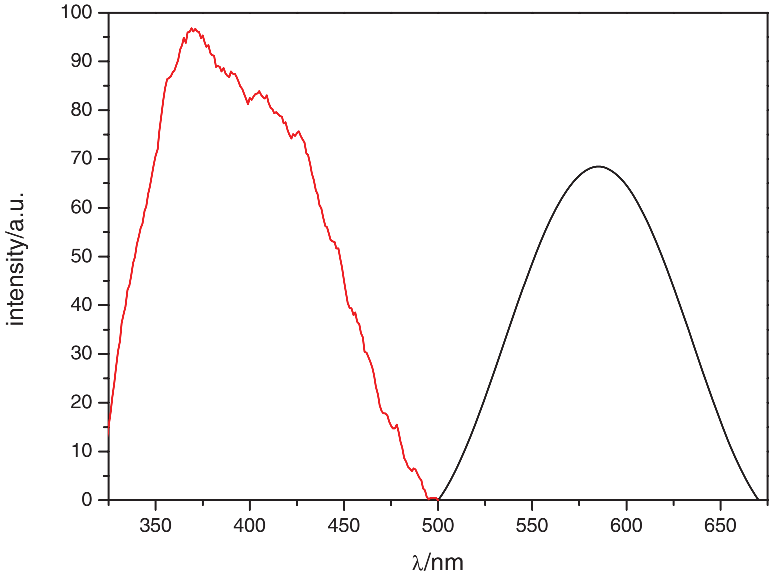


Figure 6. Excitation (on the left) and emission (on the right) spectra of Bz12 obtained in the mesophase at 45°C on first cooling cycle.

At room temperature, relatively strong interactions between the chromophores, translated into relatively strong reflections observed in the wide-angle region of the X-ray diffraction pattern of the complex Bz12 (Fig. 3(b)), could be responsible of the luminescence quenching.

Conclusions

Two new Ag(I) complexes, Bz1 and Bz12, containing N,N'-bipyridine functionalized ligand and benzoate ions as coordinated ancillary ligand, have been synthesized and fully characterized.

The single-crystal X-ray characterization of Bz1 has confirmed the formation of neutral derivatives in which the Ag(I) ion is three coordinated by the N,N-chelated bipyridine and the monodentated *o*-bonded three substituted benzoate ligands.

Moreover, complex Bz12, increases the family of Ag(I) luminescent liquid-crystalline complexes, containing a suitable functionalized benzoate, able to cooperate with the main ligand in the assembling of specific supramolecular architectures for the formation of columnar liquid-crystalline phases. Strong intermolecular contacts between chromophores are probably on the base of the luminescence quenching observed on passing from solution to the solid state. Nevertheless, a partial recovering of the luminescence is obtained when an amorphization process is induced by changing temperature. In particular, Bz12 is found to be luminescent also in its hexagonal columnar mesophase, where highly disordered molecular organization within the columns, help the chromophores to behave as isolate units.

Experimental

Materials and methods: All commercially available starting materials were used as received without further purification. Ligand 4,4′-dimethoxy-2,2′-bipyridine (*bpy-C_1*) was purchased from Sigma-Aldrich. Ligand 4,4′-bis[3,4,5-(tris-dodecyloxy)benzoyloxy methyl]-2,2′-bipyridine (*bpy-H_{12}*) was synthesized as previously reported [s1]. For the model compound, the starting material, 3,4,5-trimethoxybenzoic acid, was purchased from Sigma-Aldrich and used as received, whereas the 3,4,5-tridodecyloxybenzoic acid was synthesized as previously reported [s3].

The ^{1}H NMR spectra were recorded on a Bruker Avance AC-300 spectrometer in [D_6]DMSO, $CDCl_3$ or CD_3OD solution, using tetramethylsilane as internal standard. Elemental analyses were performed with a Perkin Elmer 2400 microanalyzer by the Microanalytical Laboratory at the University of Calabria. Infrared spectra (KBr) in the range 4000-400 cm^{-1} were recorded on a Spectrum One FT-IR Perkin Elmer spectrometer.

Mesomorphism: The textures of the mesophases were examined with a Leica DMLP polarizing microscope equipped with a Leica DFC280 camera and a CalCTec (Italy) heating stage. The thermal stability was measured on a Perkin-Elmer Thermogravimetric Analyzer Pyris 6 TGA, respectively, 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. The apparatus was calibrated with indium. Three heating/cooling cycles were performed on each sample. The powder X-Ray diffraction patterns were obtained using a Bruker AXS General Area Detector Diffraction System (D8 Discover with GADDS) with Cu-Kα radiation ($\lambda = 1.54056$ Å). The highly sensitive area detector was placed at a distance of 20 cm from the sample and at an angle ($2\theta_D$) of 14°. A CalCTec (Italy) heating stage was used to heat the samples at a rate of 5°C/min to the appropriate temperature. Measurements were performed by placing the samples in Lindemann capillary tubes with an inner diameter of 0.5 mm.

Photophysical Measurements. 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 solution absorption spectra. The examined compounds are fairly stable in solution, as demonstrated by the constancy of their absorption spectra over a week. Steady-state emission spectra were recorded on a HORIBA Jobin-Yvon Fluorolog-3 FL3-211 spectrometer equipped with a 450 W xenon arc lamp, double-grating excitation and single-grating emission monochromators (2.1 nm/mm 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. Powder samples have been prepared by placing the powder between two quartz plates, in such a position that the luminescence has been 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 a customized hot stage realized by CaLCTec s.r.l. (Rende, Italy).

Synthesis

Ag(I) 3,4,5-trimethyloxybenzoate (*p_1*): To a solution of 3,4,5-trimethyloxybenzoic acid (0.300 g, 1.414 mmol) in ethanol (25 mL) a solution of NaOH (0.057 g, 1.414 mmol) in water (5 mL) was added dropwise. The reaction mixture was stirred for 2 hours at room temperature, and then an equimolar quantity of $AgNO_3$ (0.240 g, 1.414 mmol) was added.

After stirring for another 2 hours at r.t., the white precipitate formed was filtered out and washed with ethanol to give the product (0.451 g, 85%) as a white solid. M.p. > 300°C; IR(KBr): ν_{max}/cm^{-1} 1565.9 cm^{-1} (C–O antisymm.), 1383.6 cm^{-1} (C–O symm.); ^{1}H NMR: δ_H (300 MHz, $CDCl_3$) 7.22 (2H, s), 3.82 (3H, s), and 3.74 (6H, s).

Ag(I) 3,4,5-trimethyldodecyloxybenzoate (*p₂*): To a solution of 3,4,5-trimethyldodecyloxy-benzoic acid (0.300 g, 0.444 mmol) in ethanol (25 mL) a solution of NaOH (0.015 g, 0.444 mmol) in water (5 mL) was added dropwise. The reaction mixture was stirred for 2 hours at r.t., and then an equimolecular quantity of $AgNO_3$ (0.075 g, 0.444 mmol) was added. After stirring for another 2 hours at room temperature, the white precipitate formed was filtered out and washed with ethanol to give the product (0.278 g, 82%) as a white solid. M.p. = 154°C; IR(KBr): ν_{max}/cm^{-1} 1519.9 cm^{-1} (C–O antisymm.), 1365.3 cm^{-1} (C–O symm.); ^{1}H NMR: δ_H (300 MHz, $CDCl_3$) 7.21 (2 H, s), 3.30 (6 H, m), 1.72 (6 H, m), 1.45–1.22 (54 H, overlapped peaks), and 0.88 (9 H, t, $^3J = 6.6$ Hz).

Bz1: A solution of *bpy-C₁* (0.100 g, 0.461 mmol) and precursor p_1 (0.147 g, 0.231 mmol) in $CHCl_3$ (50 ml) was stirred in a vessel protected by light for 16 hours at r.t. Then the solution was filtered under celite, the solvent was concentrated and diethyl ether was added to the solution. The precipitate formed was filtrated out and dried to give the pure complex Bz1 as a white waxy solid (0.212 g, 86%). M.p. = 172°C. Anal. Calc. for $C_{22}H_{23}AgN_2O_7$ (535.3 g·mol^{-1}): C, 49.36; H, 4.33; N, 5.23; Found: C, 49.40; H, 4.25; N, 5.42; IR(KBr): ν_{max}/cm^{-1} 1587.5 cm^{-1} (C–O antisymm.), 1385.8 cm^{-1} (C–O symm.); ^{1}H NMR: δ_H (300 MHz, $CDCl_3$) 8.70 (2 H, d, $J_{(H,H)} = 5.9$ Hz, H_6), 7.49 (2 H, d, $J_{(H,H)} = 2.3$ Hz, H_1), 7.45 (2 H, s, H_3), 6.98 (2 H, dd, $J_{(H,H)} = 5.9$ Hz, 2,3 Hz, H_5), 3.97 (3 H, s, CH_3O-benzoate), 3.92 (6 H, s, CH_3O-bipyridine), 3.89 (6 H, s, CH_3O-benzoate); and Λ_M ($C_M = 1{\cdot}10^{-5}$ mol·L^{-1}, CH_2Cl_2) = 7 cm^2·Ω^{-1}·mol^{-1}.

Bz12: A solution of *bpy-H₁₂* (0.150 g, 0.098 mmol) and precursor p_2 (0.076 g, 0.049 mmol) in $CHCl_3$ (50 ml) was stirred in a vessel protected by light for 16 hours at r.t. Then the solution was filtered under celite; the solvent was concentrated and diethyl ether was added to the solution. The precipitate formed was filtrated out and dried to give the pure complex Bz12 as a white waxy solid (0.184 g, 81%). Thermal behavior in Table 1. Anal. Calc. for $C_{141}H_{241}AgN_2O_{15}$ (2312.29 g·mol^{-1}): C, 73.24; H, 10.51; N, 1.21; Found: C, 73.15; H, 10.29; N, 1.20; IR(KBr): ν_{max}/cm^{-1} 1587.8 cm^{-1} (C–O antisymm.), 1363.5 cm^{-1} (C–O symm.); ^{1}H NMR: δ_H (300 MHz, $CDCl_3$) 8.87 (2 H, d, $J_{(H,H)} = 5.1$ Hz, H_6), 8.15 (2 H, s, H_3), 7.54 (2 H, d, $J_{(H,H)} = 4.8$ Hz, H_5), 7.38 (2 H, s, H_1), 7.30 (4 H, s, H_7), 5.45 (4 H, s, CH_2OOC), 4.02 (18 H, m, OCH_2), 1.79 (18 H, m, OCH_2CH_2), 1.50–1.25 (162 H, overlapped peaks, CH_2), 0.88 (27 H, t, $J_{(H,H)} = 6.6$ Hz, CH_3); and Λ_M ($C_M = 1{\cdot}10^{-5}$ mol·L^{-1}, CH_2Cl_2) = 3 cm^2·Ω^{-1}·mol^{-1}. Electronic Supplementary Information (ESI) available: crystallographic data and table for **Bz1**. CCDC reference number 922531.

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