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Silver Pyrazolates as Coordination-Polymer Luminescent Metallomesogens

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Abstract: Silver pyrazolates with columnar liquid-crystal phases that are stable at room temperature have been prepared by reaction of silver nitrate with 3,5-diarylpyrazolates. The complexes consist of open-chain oligomers, despite the fact that the most common structural type for homoleptic coinage metal pyrazolates is the trimeric metallacycle [M(μ-pz)]$_3$. The special characteristics of silver in forming reversible metal–ligand bonds in solution, evidenced experimentally, leads to supramolecular organizations in which the silver cations promote self-organization of the nonmesomorphic pyrazolates into helical 1D polymers that exhibit columnar mesophases. The materials are readily soluble in common organic solvents and are liquid-crystalline over a broader temperature range than their gold counterparts, which are known to form discrete cyclic trinuclear species. Thin films of the silver complexes show luminescence at room temperature. The compounds described here are the first examples of luminescent metallomesogens formed by a main-chain coordination polymer.

Keywords: liquid crystals • luminescence • metallomesogens • self-assembly • silver

Introduction

Research on coordination compounds of coinage metals ranges from basic structural studies at the molecular level to the study of supramolecular organizations and the discovery of novel properties of interest for different areas from catalysis to biomedicine or molecular electronics.[1] In coordination chemistry, pyrazolate ligands play a significant role due to their excellent bridging capability and absence of chelation, and they can yield di-, tri-, tetra-, hexa-, octanuclear, or polymeric coordination complexes. The variety of nuclearities and structures strongly depend on such factors as the nature of substituents on the pyrazole ligand, counterions, the nature of the metal center, the solvent, or noncovalent interactions.[2]

Representative examples of unique molecular architectures include those shown by homoleptic silver pyrazolates. The use of the simplest ligand, pyrazolate (pz), gave rise to an insoluble polymeric material[3,4] [Ag(μ-pz)]$_n$, and changes in the synthetic method led to a trimeric cyclic structure [Ag(μ-pz)]$_3$.[3] In the case of substituted pyrazoles, although a tetrameric structure has been described for the complex with 3,5-di(*tert*-butyl)pyrazolate ligands [Ag(μ-3,5-*t*Bupz)]$_4$,[5] the most common structural type is the trimeric ring structure.[6–9] The trimeric structure consists of a nine-membered Ag$_3$N$_6$ metallacycle with a planar array of *N*,*N*′-bridging pyrazolates and linearly coordinated silver ions. These materials were recently reported to show fascinating properties as a consequence of their tunable supramolecular organization. For example, optical properties such as photoluminescence,[8,10] electronic properties such as charge transfer in columnar stacks,[11] and chemical properties such as gas adsorption in functional porous networks have been reported.[12]

Our aim was to develop novel functional soft materials with silver pyrazolates by using appropriate ligands to yield columnar liquid crystals,[13] thus obtaining metal-containing

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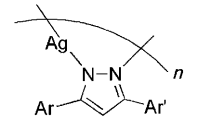
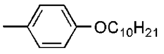
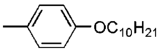
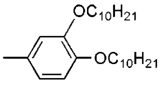
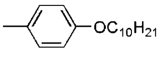
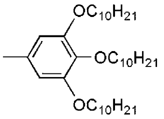
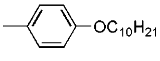
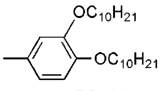
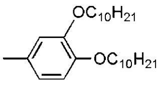
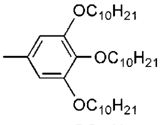
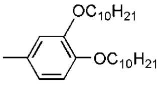
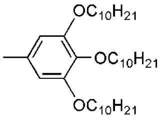
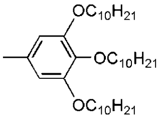
liquid crystals (metallomesogens) that combine columnar order with advantages such as the solubility and processability of soft materials.[14] Reports of columnar mesophases in silver complexes are scarce and limited to ionic complexes with stilbazole,[15] pyridine,[16] or bipyridine ligands.[17] The mesomorphic properties of these materials are very dependent on the nature of the counterion and, in most cases, the mesophase is not stable at room temperature.

In an effort to obtain liquid crystallinity at room temperature with homoleptic silver pyrazolates, we focused on polycatenar 3,5-diarylpyrazoles. Indeed, gold(I) complexes of these ligands are trinuclear metallacycles $[Au(\mu\text{-pz})]_3$ that show thermodynamically stable columnar mesophases.[18,19] More recently, we have shown that the polycatenar pyrazolates are compatible with different coordination geometries and room-temperature mesophases have been described for coordination compounds with square-planar rhodium(I) or tetrahedral zinc(II); thus, these ligands are very useful for promoting columnar mesomorphism.[20,21]

We describe herein a number of silver metallomesogens that exhibit columnar liquid-crystal phases and also report on the different and unexpected behavior compared to the analogous gold complexes. The ligands are nonmesomorphic 3,5-diarylpyrazolates substituted at different positions of the phenyl rings with *n*-decyloxyl chains (Table 1). We found that silver(I) promotes self-organization in columnar mesophases at room temperature and that these phases are stable over wide temperature ranges. Studying the mesophases by using XRD allowed us to propose models for the supramolecular organization of the materials. The different behavior observed in comparison with the analogous gold(I) complexes is also discussed. Our observations led us to propose that these compounds do not consist of cyclic trinuclear complexes (CTC), as one would expect from previous structural work on silver pyrazolates, but are open-chain oligomeric species that self-organize to form very stable columnar mesophases. These materials show luminescence in the columnar phases at room temperature. This work adds to the very few examples of metallomesogens formed by main-chain coordination polymers that show columnar mesophases,[22] and is, to the best of our knowledge, the first such example to exhibit luminescence.

Table 1. Molecular structures of silver pyrazolates with different chain substitution at the Ar and Ar′ phenyl rings.



	Ar	Ar′
$[Agpz^{1,1}]_n$		
$[Agpz^{2,1}]_n$		
$[Agpz^{3,1}]_n$		
$[Agpz^{2,2}]_n$		
$[Agpz^{3,2}]_n$		
$[Agpz^{3,3}]_n$		

Results and Discussion

Synthesis and characterization: The complexes were synthesized by mixing equimolar amounts of the pyrazole ligand, triethylamine, and silver nitrate in acetone. The mixture was heated to slightly above room temperature to dissolve the polycatenar pyrazole ligands. The silver complexes were isolated as ivory solids or beige pastes that are readily soluble in common organic solvents, such as THF, dichloromethane, chloroform, toluene, cyclohexane, and hexane.

Elemental analysis was consistent with a 1:1 ligand-to-metal stoichiometry $[Agpz^{x,y}]_n$, and evidence for NH stretching bands was not observed in the FTIR spectra of neat samples. The ^{1}H NMR spectra of solutions of the complexes in chloroform show a shift in the peaks in the aromatic region with respect to the starting ligand. Moreover, NH peaks ($\approx$11–13 ppm in the ligand) were not observed, that is, metal complexation to neutral 1*H*-pyrazoles does not occur.[23]

The aromatic regions of the ^{1}H NMR spectra contain one set of ligand signals, and these are shifted upfield with respect to those of the corresponding 1*H*-pyrazole ligand. This trend is independent of the chain substitution in the pyrazolate ligand, be it symmetric ($pz^{1,1}$, $pz^{2,2}$, $pz^{3,3}$) or nonsymmetric ($pz^{2,1}$, $pz^{3,1}$, and $pz^{3,2}$). In contrast, four sets of signals were observed for the gold(I) complex of nonsymmetric pyrazolate $pz^{3,2}$, a trinuclear cyclic compound $[Au(\mu\text{-}pz^{3,2})]_3$ that consisted of a mixture of two geometrical isomers (C_3 and C_∞ symmetric).[18]

The different NMR behavior of the silver complexes with respect to the gold complexes can be explained by two scenarios. Firstly, one can assume that $[Ag(\mu\text{-}pz^{x,y})]_3$ cyclic trinuclear complexes (CTC) are formed (as in the case of the gold compounds), but of the two possible isomers only the C_3-symmetric form is obtained. The second possibility is to consider that silver–pyrazolate interactions are more labile than gold–pyrazolate bonds and, in solution, ligand–metal exchange through a coordination–decoordination process that is faster than the NMR timescale. In this case only a pyrazolate–silver intermediate, in which silver is in equilibrium between the two nitrogen atoms, is observed.

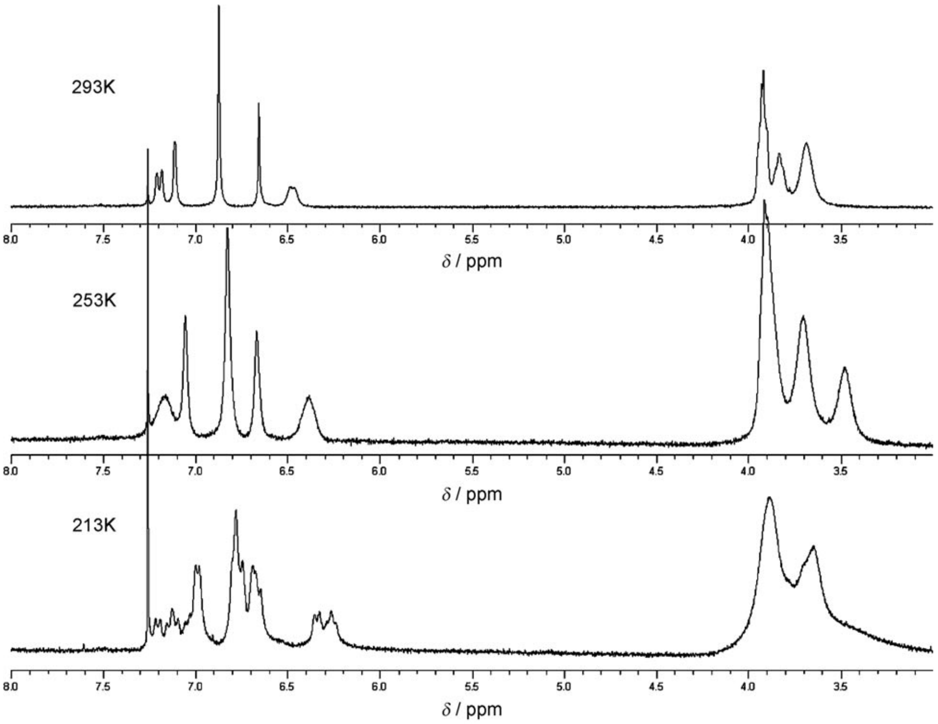


Figure 1. Variable-temperature ^{1}H NMR spectra for $[\text{Agpz}^{3,2}]_n$ in CDCl_3.

To gain further insight into this issue, a ^{1}H NMR spectroscopy experiment was carried out on $[\text{Agpz}^{3,2}]_n$ at low temperatures (Figure 1). Splitting of all aromatic signals was observed on lowering the temperature to 213 K. The splitting of the signal corresponding to the proton at the 4-position of the pyrazole ring ($\delta = 6.67$ ppm) into three or more signals indicates that nonsymmetric species with a nuclearity greater than one exist. It can be concluded that the silver complexes must be labile in solution at room temperature and undergo ligand exchange that is rapid on the NMR timescale. Therefore, in this case it cannot be stated that only the C_3 isomer is obtained, as previously proposed,[24] but that at room temperature a rapid equilibrium exists and intermediate ligand–metal exchange can be observed. In contrast, dynamic behavior was not observed for the gold complexes. From our observations we propose that cyclic trinuclear species do not exist for these silver pyrazolates.

Other differences in the spectra were observed. For example, like for the gold CTCs the signal corresponding to the aromatic protons in the *ortho* position of the 3,4-disubstituted phenyl ring appear at lower field than those in the silver complexes ($\delta = 7.37$–7.44 ppm in gold complexes and $\delta = 7.21$ ppm in silver complexes). On lowering the temperature, splitting was observed for the silver complexes but the signal was not shifted to lower field, an observation that may be consistent with the presence of acyclic oligomeric species.

Signal splitting was not observed at room temperature at different concentrations, that is, the effect observed on lowering the temperature was not due to intermolecular aggregation. This finding supports the proposal that at room temperature an equilibrium exists and lowering the temperature leads to freezing of the equilibrium.

Several reports have been published on the lability of Ag–N bonds in ^{1}H NMR studies in solution of ionic complexes of neutral pyrazoles[23] or poly(pyrazolyl)methanes.[25] In contrast, only one recent work by Dias et al. concerned the reversibility of silver pyrazolates, which behaved as single mono-, di-, or polynuclear species in a vapor-pressure osmometry study on $[\text{Ag}(\mu\text{-}(3,5\text{-}(\text{CF}_3)_2\text{pz}))]_3$, although the authors did not propose an equilibrium between open-chain oligomers.[26]

The MALDI-TOF mass spectra showed several peaks corresponding to fragments with a stoichiometry of $[\text{Ag}_{n+1}\text{pz}^{x,y}{}_n]$, that is, the molecular ion corresponding to the elemental composition $[\text{Ag}_n\text{pz}^{x,y}{}_n]$ plus a silver ion. This indicates that the material tends to ionize as $[M+\text{Ag}]^+$ oligomers of different nuclearities (see the Experimental Section). In one case, peaks for up to a heptanuclear oligomer $[\text{Ag}_7\text{pz}^{2,1}{}_6]$ could be observed (Figure 2). Surprisingly, none of the peaks corresponded to the $[\text{Ag}_3\text{pz}^{x,y}{}_3]$ stoichiometry. In contrast, MALDI-TOF MS of the gold CTCs under the same experimental conditions always gave the $[\text{Au}_3\text{pz}^{x,y}{}_3]$ peak, a finding that further supports the polymeric character of the silver-containing materials. Attempts to characterize the coordination polymers by gel permeation chromatography only gave a signal with a similar retention time to that of the pyrazole ligand.

Masciocchi et al. reported different structures for silver pyrazolates (polymeric or cyclic trinuclear) depending on the synthetic method used.[3] We also synthesized $[\text{Agpz}^{3,2}]_n$ by using the method reported by Dias et al. for silver CTCs,[9] with Ag_2O as the source of silver and base, and toluene as solvent. The resulting material gave the same ^{1}H NMR spectrum as in Figure 1. Therefore, we conclude that in our case the synthetic method did not affect the final structure. It is likely that the more labile nature of silver and the steric bulk of the substituents in the 3,5-positions of the pyrazolate backbone control the nuclearity and the cyclic/open-chain nature of the molecular structure.

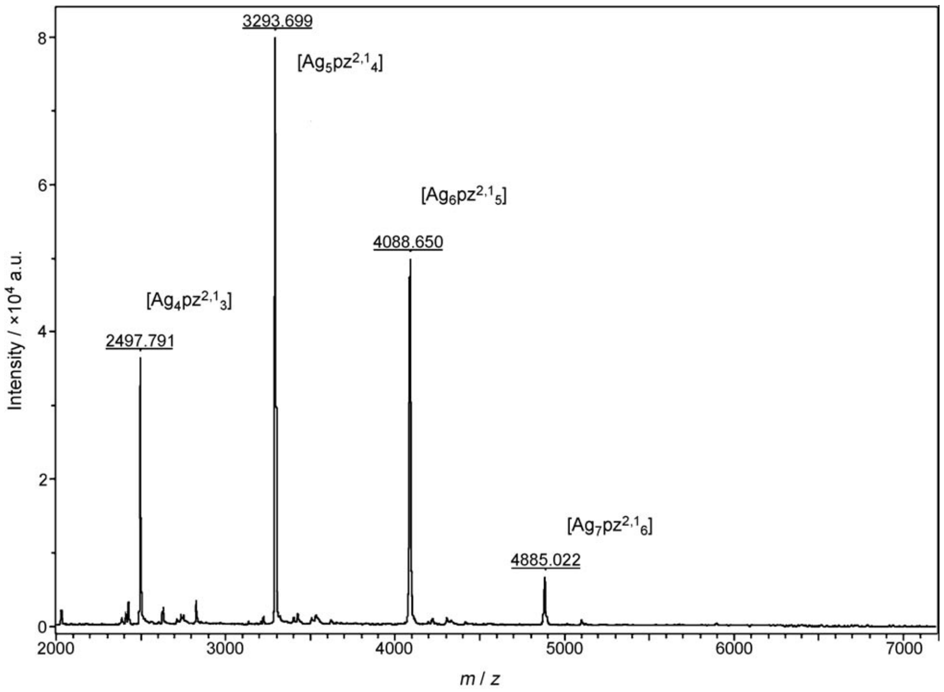


Figure 2. MALDI-TOF MS of $[Agpz^{2,1}]_n$.

Thermal and self-organization properties: All silver pyrazolate complexes exhibited liquid-crystalline behavior except for $[Agpz^{1,1}]_n$. Studies of the thermotropic behavior of different batches showed the same properties, which indicates that although the material can be oligomeric/polymeric, the thermal properties are completely reproducible.

The textures of the mesophases by polarizing optical microscopy are birefringent pseudofocal conic textures with linear defects that are typical of hexagonal columnar mesophases (Figure 3). In the case of $[Agpz^{3,1}]_n$, leaflike textures without hexagonal symmetry grew on cooling the isotropic liquid, which indicates that the mesophase may not belong to a hexagonal symmetry (Figure 3b). Further changes were not observed on cooling any of the samples to room temperature. A decrease in the clearing points was found on increasing the number of chains (Table 2), a finding consistent with the behavior observed in columnar liquid crystals that contain polycatenar pyrazolates, such as the analogous gold complexes.[19] However, the liquid-crystalline phases of the silver analogues are considerably more stable than those of the gold CTCs. For example, $[Aupz^{2,2}]_3$ is a crystalline solid that melts to a columnar mesophase at 59 °C and clears at 64 °C to the isotropic liquid. In contrast, $[Agpz^{2,2}]_n$ shows a columnar mesophase between room temperature and 143 °C.

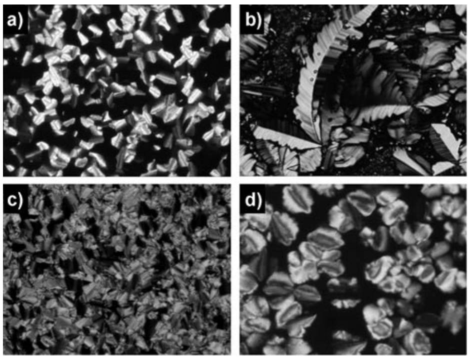


Figure 3. Microphotographs of the mesophases observed for a) $[Agpz^{2,1}]$ at 55 °C, b) $[Agpz^{3,1}]$ at 115 °C, c) $[Agpz^{2,2}]$ at RT, and d) $[Agpz^{3,2}]$ at 92 °C.

Differential scanning calorimetry cycles are reproducible and decomposition was not observed either at the mesophase temperatures or at the clearing point, except for $[Agpz^{2,1}]_n$, which underwent partial decomposition at the clearing point (170 °C). We observed that when this temperature was reached, further cooling and heating cycles showed a monotonic decrease in the temperature and enthalpy of the mesophase-to-isotropic liquid transition. However, no volatile decomposition product was observed in the thermogravimetric analysis up to 310 °C. The compounds also showed good stability under standard illumination conditions.

Table 2. Thermal and thermodynamic properties.

	Phase transitions[a] T_{peak} [°C]	ΔH [J g^{-1}]	ΔH[b] [kJ (mol$_{Agpz}$)$^{-1}$]	ΔS[b] [J (mol$_{Agpz}$)$^{-1}$ K^{-1}]
$[Agpz^{1,1}]_n$	Cr 96 I	8.4	5.4	14.6
$[Agpz^{2,1}]_n$	Col$_h$ 170 I (decomp.)[c]	3.2	2.5	5.6
$[Agpz^{3,1}]_n$	Col$_r$ 124 I	3.9	3.7	9.3
$[Agpz^{2,2}]_n$	Col$_h$ 143 I	3.8	3.6	8.6
$[Agpz^{3,2}]_n$	Col$_h$ 93 I	11.0	12.2	33.3
$[Agpz^{3,3}]_n$	Col$_h$ 61 I	5.5	6.9	20.6

[a] Cr: crystalline phase, Col$_h$: hexagonal columnar mesophase, Col$_r$: rectangular columnar mesophase, I: isotropic liquid. [b] Calculated value per repeating unit. [c] Unreproducible DSC traces above this temperature.

X-ray diffraction studies on $[Agpz^{2,1}]_n$, $[Agpz^{3,1}]_n$, $[Agpz^{2,2}]_n$, $[Agpz^{3,2}]_n$, and $[Agpz^{3,3}]_n$ confirmed that these compounds are all liquid-crystalline at room temperature (Table 3, Figure 4). Compounds $[Agpz^{2,1}]_n$, $[Agpz^{2,2}]_n$, $[Agpz^{3,2}]_n$, and $[Agpz^{3,3}]_n$ show reflections in the small-angle region that are typical of a hexagonal columnar symmetry. The X-ray patterns of the mesophases of the complexes show a set of four (two in the case of $[Ag(pz^{2,1})]_n)$ sharp maxima in the small-angle region, and these correspond to

Table 3. Room-temperature XRD data.

	Mesophase	Cell parameters	d_{obsd} [Å]	*hk*	d_{calcd} [Å]
$[\mathrm{Agpz}^{2,1}]_n$	$\mathrm{Col_h}$	$a=30.7$ Å	26.4	10	26.6
		$S=816$ Å^2	15.5	11	15.3
$[\mathrm{Agpz}^{3,1}]_n$	$\mathrm{Col_r}$	$a=21.3$ Å	28.9	02	29.0
		$b=58$ Å	19.9	11	20.0
		$S=1235$ Å^2	14.3	04 (or 13)	14.5 (or 14.3)
			10.9	20	10.7
			10.2	15 (or 22)	10.2 (or 10.0)
			8.5	24	8.6
			7.7	17	7.7
			7.0	31	7.0
			6.05	35	6.06
$[\mathrm{Agpz}^{2,2}]_n$	$\mathrm{Col_h}$	$a=32.8$ Å	28.1	10	28.4
		$S=932$ Å^2	16.3	11	16.4
			13.9	20	14.2
			10.9	21	10.7
			3.6		
$[\mathrm{Agpz}^{3,2}]_n$	$\mathrm{Col_h}$	$a=30.5$ Å	26.4	10	26.4
		$S=805$ Å^2	15.4	11	15.2
			12.9	20	13.2
			10.1	21	10.0
			3.8		
$[\mathrm{Agpz}^{3,3}]_n$	$\mathrm{Col_h}$	$a=31.2$ Å	26.7	10	27.0
		$S=842$ Å^2	15.8	11	15.6
			13.3	20	13.5
			10.3	21	10.2
			3.9		

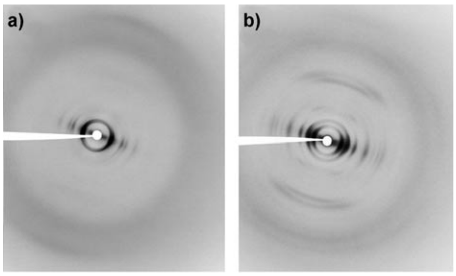


Figure 4. XRD patterns at room temperature for the mesophase of a) $[\mathrm{Agpz}^{2,2}]_n$ and b) $[\mathrm{Agpz}^{3,1}]_n$.

reciprocal spacings in the ratio $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$. These peaks were assigned to the (10), (11), (20), and (21) reflections from a two-dimensional hexagonal lattice (Table 3). These patterns are consistent with a hexagonal columnar mesophase in which the column axes are located at the nodes of the two-dimensional lattice and oriented perpendicular to the plane of this lattice. In the large-angle region a broad diffuse halo at 4.3–4.6 Å was observed and is related to the short-range correlations between the molten hydrocarbon chains. The parameter of the hexagonal lattice, *a*, calculated from the low-angle reflections, remains almost constant regardless of the number of chains in the pyrazole ligand. This finding is consistent with the results obtained for other columnar liquid crystals and is related to the fact that a higher number of aliphatic chains implies a greater spatial requirement out of the molecular plane but does not increase the column diameter, which depends mainly on the chain length. In fact the hexagonal lattice constant *a* decreases slightly from $[\mathrm{Agpz}^{2,2}]_n$ to $[\mathrm{Agpz}^{3,2}]_n$.

In the XRD patterns of thermally treated and then mechanically aligned samples of some complexes, some diffuse scattering is visible at high diffraction angles in the meridian region (Figure 4a). This scattering is related to an additional modulation of the electronic density, which corresponds to intracolumnar short-range correlations along the column axis at distances of about 3.6–3.9 Å. The distance of 3.6–3.9 Å could be interpreted in terms of a repeat stacking distance between trimeric complexes. However, very simple calculations based on this hypothesis would lead to an unreasonable mesophase density of about $2\,\mathrm{g\,cm^{-3}}$. A more reasonable density of about $1\,\mathrm{g\,cm^{-3}}$ is obtained if a column stratum of 3.6–3.9 Å thickness contains between 1.5 and two silver atoms and the same number of pyrazolate ligands. However, a dimeric structure is not consistent with the linear coordination geometry of silver(I) and the sp^2 hybridization of the nitrogen atoms. Therefore, the X-ray results are not consistent with stacking of discrete molecules with a fixed composition. Instead, on the basis of the NMR and MS data (see above), the columns are probably formed by mixtures of oligomers, and the diffuse scattering at 3.6–3.9 Å arises from short-range correlations between the silver atoms and/or the aromatic rings along the column axis. The short-range nature of these correlations is revealed by the broad, diffuse character of the aforementioned scattering band. This phenomenon is probably connected to the polymeric nature of the complexes and the fact that the correlations are only short-range must be related to the polydispersity of the different oligomeric species.

To understand the self-organization in the column we must take into account the linear two-coordinate geometry of silver(I) in homoleptic pyrazolate complexes and the versatility of torsion angles between pyrazolate ligands in a pz-Ag-pz moiety. For the gold CTC all pz-Au-pz bonds are in a *cisoid* conformation (torsion angle between pyrazolate units ca. 0°) in order to form a closed ring. In our silver complexes, however, closed rings stacked at 3.6–3.9 Å can be ruled out due to the density being too high (see above). If open species are formed then the torsion angles should be larger than 0°, a situation that would stretch the column and decrease the packing density, which would be in accordance with the column parameters measured.

The opposite situation would be a *transoid* conformation, that is, all torsion angles between pyrazolate units are 180°. The all-*transoid* arrangement of an open oligomer would not be compatible with the bulky substituents at the 3- and 5-positions of the pyrazole ligands for steric reasons, as observed in 3D models. Therefore, intermediate pz-Ag-pz torsion angles are believed be present along the column. Staggered conformations (e.g., torsion angles close to 90°) are present in the single-crystal structures of tetranuclear silver and gold pyrazolates with bulky *tert*-butyl substituents at the 3- and 5-positions $[\mathrm{Ag}(\mu\text{-}3,5\text{-}t\mathrm{Bupz})]_4$[5] and $[\mathrm{Au}(\mu\text{-}3,5\text{-}t\mathrm{Bupz})]_4$.[27] Different torsion angles that are close to *cisoid* or *transoid* conformations have also been observed in a hexanuclear gold complex with phenyl groups at the 3- and 5-positions, namely, [Au(μ-3,5-Phpz)]$_6$.[6] Moreover, staggered conformations with torsion angles around 90° have also been described for 1D polymeric supramolecular structures built from hydrogen bonding (catemers) of metal-free 1*H*-pyrazoles,[28] as found in 3-carboxymethyl-5-phenyl-1*H*-pyrazole.[29] Finally, the single-crystal structure of the only silver pyrazolate polymer described, [Ag(μ-pz)]$_n$, has been solved to be a helical chain in which silver is linearly coordinated by two pyrazolate ligands with N-Ag-N angles of 170°, regular pz-Ag-pz torsion angles of 120° (that is, staggered closer to *transoid* conformation than to *cisoid* conformation), and intrachain Ag···Ag distances between 3.25 and 3.37 Å.[4] It is quite possible that, taking into account the bulky polyalkoxyphenyl substituents in the 3- and 5-positions of the pyrazole, one open oligomer could stack along a column if we consider a pz-Ag-pz torsion angle close to a staggered conformation. It is also quite reasonable to consider that, given the measured electronic density modulation of 3.6–3.9 Å, the torsion angle may be regular along one oligomer. One possible arrangement consistent with Ag_2pz_2 units per columnar stratum is depicted in Figure 5. In this way polymeric [N-Ag-N] chains are formed by the silver ions and the pyrazolate rings mutually rotated by almost 90°, and thus a helical conformation (a 2:1 helix) is generated. The conformational flexibility of the pz-Ag-pz torsion angles, as well as some flexibility of the linear N-Ag-N coordination would allow the stacking distance to vary slightly depending on the ligand. This model will be related to the helical polymeric structure observed for [Ag(μ-pz)]$_n$.[4] Other possible structures, such as a flat chain with alternating *cisoid–transoid* conformations, as found in the silver imidazolate polymer [Ag(μ-im)]$_n$,[30] would not be fully consistent with the measured electronic density modulation of 3.6–3.9 Å.

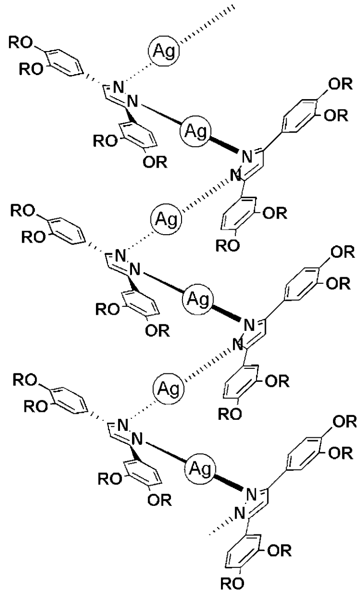


Figure 5. Schematic representation of a 2:1 helix.

In the case of [Agpz^{3,1}]$_n$, which contains the most asymmetric ligand, the X-ray patterns are more complex than those of the rest of the series. The diffractogram contains a large number of sharp maxima that fit a highly organized two-dimensional rectangular lattice, which indicates that the mesophase is columnar rectangular (Table 3). In addition, the patterns contain some diffuse halos in the medium- and high-angle regions, and these are concentrated in the meridian region for the aligned sample (Figure 4b). Some of these bands have their intensity maximum in the meridian direction, whereas other bands split off the meridian. The existence of off-meridian scattering suggests the existence of helical order within the columns and supports the model proposed for the hexagonal columnar mesophase of the other compounds in the series. For [Agpz^{3,1}]$_n$, the diffuse bands correspond to electronic density modulations along the column axis with periods of about 14, 7, and 4.2 Å. If we assume that the scattering maximum at 14 Å corresponds to the helix period and there are two columns per rectangular cell unit, a density close to 1 g cm^{-3} is predicted if five pyrazolate rings and five silver ions are contained in a column length of 14 Å. The presence of an additional scattering maximum at 7 Å is consistent with a 5:2 helix. Thus the helix period (14 Å) must contain two helix turns, and two and a half [Agpz^{3,1}] units are needed to complete each helix turn. This is possible if the torsion angle pz-Ag-pz is smaller than for the 2:1 helix and closer to a *cisoid* conformation. The scattering at 4.2 Å arises from intramolecular correlations in the polymer chain along the column axis. In the X-ray patterns of the hexagonal columnar mesophases the diffuse band at 3.7–3.9 Å is very broad and weak, whereas the sharper and stronger meridian bands in the X-ray patterns of [Agpz^{3,1}]$_n$ suggest a higher degree of intracolumnar order in the rectangular columnar mesophase of this compound.

The composition of the oligomers could vary depending on the compound in question. The fact that a highly ordered helical structure for [Agpz^{3,1}]$_n$ is observed by XRD could be related to the presence of oligomers of higher molecular weight than for the other compounds. This situation would extend the intracolumnar order to longer distances and produce higher intensity X-ray scattering in the meridian direction of the pattern.

Luminescence properties: All compounds show luminescence in the bulk at room temperature. Measurements were made on thin films, which were prepared by sandwiching the neat compound between two quartz pellets, heating to the isotropic liquid state, and cooling to room temperature. The columnar-mesophase texture of the resulting films was detected by using polarizing optical microscopy.

The emission spectra consisted of structured bands in the region $\lambda = 350$–500 nm (Figure 6), and these were similar to those described for gold complexes with 3-alkoxyphenylpyrazolate or 3,5-diphenylpyrazolate ligands, which appeared in the $\lambda = 390$–500 nm range.[31] On the other hand,

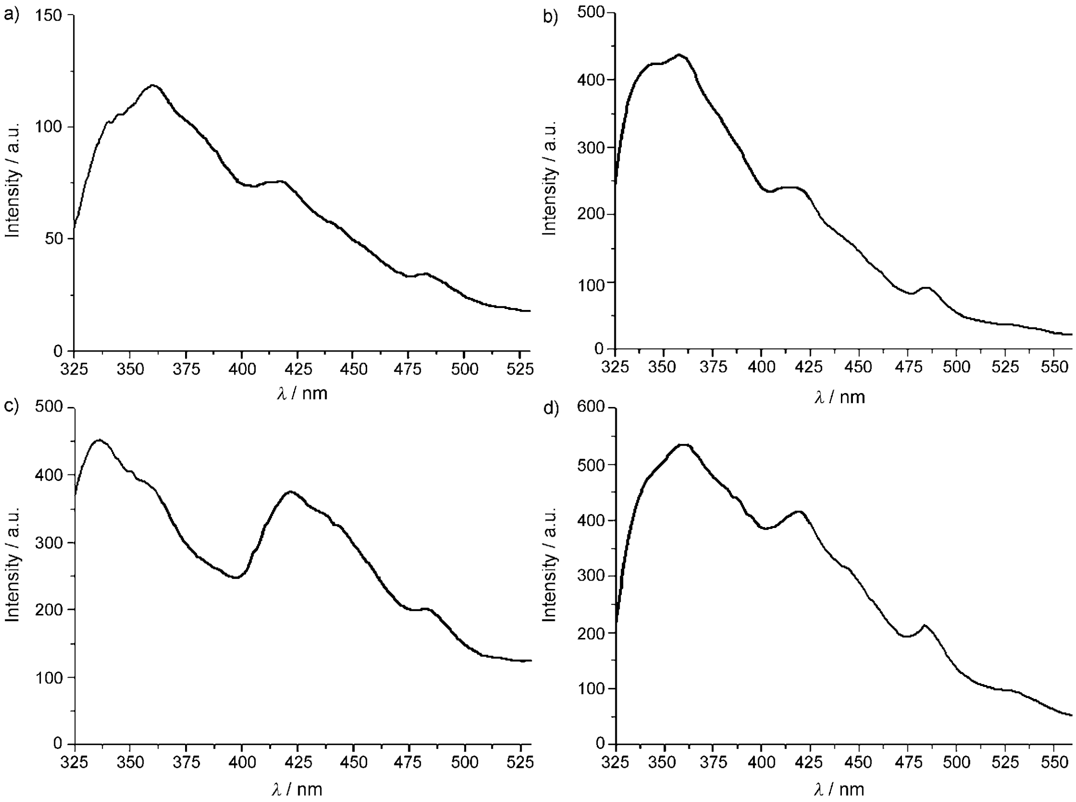


Figure 6. Emission spectra of a) $Agpz^{2,1}$, b) $Agpz^{3,1}$, c) $Agpz^{3,2}$, and d) $Agpz^{3,3}$; excitation at $\lambda = 300$ nm.

thin films of polycatenar 3,5-diarylpyrazole ligands have been reported to show emission at $\lambda = 340$–350 nm.[21,32] Based on these observations, the complex emission band of the silver pyrazolates has been tentatively attributed to both intraligand and ligand-to-metal charge transfer (LMCT) transitions involving the π electronic ground state of the ligand.

The type of substitution and number of alkoxyl chains does not significantly affect the emission spectra. Only changes in the relative intensities of the complex emission band were detected. Metal-centered emission bands in the $\lambda = 600$ nm region[10] were not detected under these experimental conditions.

Conclusion

Novel metallomesogenic polymers consisting of coordination complexes of silver with 3,5-diarylpyrazolate ligands have been described. These silver complexes behave very differently from the analogous gold pyrazolate complexes. Whereas gold complexes are constituted by discrete cyclic trinuclear molecules, the silver pyrazolates are open 1D polymers or oligomers. This structure is a result of the fact that Ag–N bonds are more labile than Au–N bonds, as observed in the experiments in solution, in which there is clearly equilibrium exchange between silver and pyrazolate. This dynamic behavior of silver allows self-assembly of the pyrazolates to give open oligomers that self-organize into columnar mesophases with a broad stability range. In this way silver is not analogous to but much more efficient than gold in promoting liquid-crystalline columnar organizations with promesogenic pyrazolates. This behavior is an example of coordination-driven self-assembly of a functional unit in a controlled columnar liquid-crystalline superstructure with luminescent properties.

Experimental Section

Reactions were carried out under a N_2 atmosphere by using Schlenk techniques. Silver nitrate (Aldrich), triethylamine (Scharlau), dry acetone, and methanol (Scharlab) were used without further purification. Dichloromethane was dried over CaH_2 and distilled under N_2 prior to use. Polycatenar pyrazole ligands were prepared as previously reported.[21,33]

Elemental analysis was performed by using a Perkin–Elmer 240C microanalyzer. IR spectra were measured as Nujol mulls on NaCl disks by using a Nicolet Avatar FTIR instrument. ^1H NMR spectra were recorded by using Bruker ARX 300 or Avance 400 spectrometers. Mass spectra were obtained by MALDI-TOF by using a Bruker MicroFlex instrument. Mesomorphic behavior and transition temperatures were determined by using an Olympus BH-2 polarizing microscope equipped with a Linkam THMS 600 hot-stage central processor and a CS196 cooling system. Differential scanning calorimetry (DSC) was carried out by using a DSC Q20 from TA Instruments with samples sealed in aluminum pans and a scanning rate of 10 °C min^{-1} under a nitrogen atmosphere. The apparatus was calibrated with indium (156.6 °C, 28.4 J g^{-1}) as standard. Powder X-ray diffraction experiments were carried out by using a pinhole camera (Anton Paar) operating with a Ni-filtered $Cu_{K\alpha}$ beam. The sample was held in a Lindemann glass capillary (0.9 mm diameter) and thermally treated with a variable-temperature attachment. The X-ray patterns were collected on flat photographic film. Fluorescence studies were conducted by using a Perkin–Elmer LS50B fluorometer by front-face detection.

General procedure for the preparation of $[Agpz^{x,y}]_n$ complexes: The corresponding pyrazole ligand (0.15 mmol) and triethylamine (0.15 mmol) were stirred in dry acetone (20 mL) at 40 °C for 15 min. The solution was added dropwise to a solution of silver nitrate (0.15 mmol) in acetone (20 mL). The mixture was stirred in darkness at 45 °C for 3 h and evaporated to dryness. The resulting mixture was stirred in dichloromethane and the solid was filtered off. Concentration to a small volume (2 mL) and cooling with liquid nitrogen gave an ivory precipitate that was purified by washing several times with small amounts of methanol. The product was dried under vacuum.

Compound $[Agpz^{1,1}]_n$: Yield: 55 %. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.81$ (t, $J = 3.6$ Hz, 6H), 1.22–1.41 (m, 28H), 1.68–1.72 (m, 4H), 3.80 (t, $J = 6.4$ Hz, 4H), 6.54 (s, 1H), 6.60 (m, AA′XX′, 4H), 7.49 ppm (m, AA′XX′, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.1$, 22.7–31.9, 67.9, 100.1, 114.6, 125.8, 127.4, 154.0, 158.9 ppm; IR (Nujol): $\tilde{\nu} = 1613$, 1504 (C=N, ArC−C), 1248 cm^{-1} (C-O-C); MS (MALDI$^+$, dithranol): m/z: 3305.3 $[Ag_6pz_5]^+$, 2665.2 $[Ag_5pz_4]^+$, 2025.2 $[Ag_4pz_3]^+$, 1387.1 $[Ag_3pz_2]^+$, 1279.2 $[Ag_2pz_2]^+$, 1173.4 $[Agpz_2]^+$, 639.5 $[Agpz]^+$; elemental analysis calcd (%) for $C_{35}H_{51}AgN_2O_2$: C 65.7, H 8.0, N 4.4; found: C 65.8, H 7.95, N 4.4.

Compound $[Agpz^{2,1}]_n$: Yield: 58 %. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.87$ (t, $J = 7.2$ Hz, 9H), 1.23–1.52 (m, 42H), 1.73–1.83 (m, 6H), 3.90–3.95 (m, 6H), 6.57 (d, $J = 8.8$ Hz, 1H), 6.65 (s, 1H), 6.69 (m, AA′XX′, 2H), 7.14 (d, $J = 2.0$ Hz, 1H), 7.23 (dd, $J = 8.4$ Hz, $J = 2.0$ Hz, 1H), 7.58 ppm (m, AA′XX′, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.1$, 22.7–31.9, 67.9, 69.1, 100.4, 113.6, 114.6, 114.7, 118.4, 122.1, 125.2, 127.4, 141.4, 146.6, 149.2, 159.5 ppm; IR (Nujol): $\tilde{\nu} = 2923$, 2853 (C−H), 1612, 1576, 1541, 1524, 1491 (C=N, ArC−C), 1248 cm^{-1} (C-O-C); MS (MALDI$^+$, DCTB): m/z: 4885.0 $[Ag_7pz_6]^+$, 4088.6 $[Ag_6pz_5]^+$, 3293.7 $[Ag_5pz_4]^+$, 2497.8 $[Ag_4pz_3]^+$; elemental analysis calcd (%) for $C_{45}H_{71}AgN_2O_3$: C 67.9, H 9.0, N 3.5; found: C 67.8, H 9.3, N 3.5.

Compound $[Agpz^{3,1}]_n$: Yield: 65 %. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.85$ (t, $J = 6.8$ Hz, 12H), 1.25–1.49 (m, 56H), 1.67–1.80 (m, 8H), 3.72 (m, 4H), 3.91 (m, 4H), 6.63 (m, AA′XX′, 2H), 6.67 (s, 1H), 6.87 (s, 2H), 7.55 ppm (m, AA′XX′, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.1$, 22.7–32.0, 67.9, 68.8, 73.3, 100.7, 104.1, 114.6, 127.0, 128.6, 129.4, 138.2, 148.0, 153.5, 159.2 ppm; IR (KBr): $\tilde{\nu} = 2923$, 2853 (C−H), 1613, 1582, 1497, 1488 (C=N, ArC−C), 1249 cm^{-1} (C-O-C); MS (MALDI$^+$, DCTB): m/z: 3917.0 $[Ag_5pz_4]^+$, 2964.9 $[Ag_4pz_3]^+$, 2012.2 $[Ag_3pz_2]^+$, 953.9 $[Agpz]^+$, 846.0 $[Hpz]^+$; elemental analysis calcd (%) for $C_{55}H_{91}AgN_2O_4$: C 69.4, H 9.6, N 2.9; found: C 69.6, H 9.4, N 3.1.

Compound $[Agpz^{2,2}]_n$: Yield: 75 %. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 0.85–0.90 (m, 12H), 1.26–1.49 (m, 56H), 1.73 (m, 4H), 1.81 (m, 4H), 3.87 (t, $J = 6.8$ Hz, 4H), 3.93 (t, $J = 6.8$ Hz, 4H), 6.54 (d, $J = 8.0$ Hz, 2H), 6.63 (s, 1H), 7.13 (d, $J = 2.0$ Hz, 2H), 7.23 ppm (dd, $J = 8.4$ Hz, $J = 1.6$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.0$, 22.6–31.9, 68.9, 69.1, 100.5, 112.4, 113.5, 118.2, 126.4, 142.4, 144.2, 149.3, 155.2 ppm; IR (KBr): $\tilde{\nu} =$ 2922, 2853 (C−H), 1607, 1585, 1523, 1493 (C=N, ArC−C), 1258 cm^{-1} (C-O-C); MS (MALDI$^+$, DCTB): m/z: 3917.5 $[Ag_5pz_4]^+$, 2964.0 $[Ag_4pz_3]^+$, 2012.3 $[Ag_3pz_2]^+$, 1904 $[Ag_2pz_2]^+$, 1798.4 $[Agpz_2]^+$, 1059.7 $[Ag_2pz]^+$, 951.9 $[Agpz]^+$, 846.1 $[Hpz]^+$; elemental analysis calcd (%) for $C_{55}H_{91}AgN_2O_4$: C 69.4, H 9.6, N 2.9; found: C 69.7, H 9.4, N 2.9.

Compound $[Agpz^{3,2}]_n$: Yield: 60 %. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.81$ (m, 15H), 1.27–1.51 (m, 15H), 1.69–1.84 (m, 70H), 3.70 (m, 4H), 3.84 (m, 2H), 3.93 (m, 4H), 6.49 (d, $J = 8.0$ Hz, 1H), 6.67 (s, 1H), 6.89 (s, 2H), 7.13 (s, 1H), 7.21 ppm (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.1$, 22.7–31.9, 68.9, 73.3, 100.8, 104.0, 112.3, 113.4, 117.8, 125.8, 128.2, 138.1, 149.1, 149.4, 153.5, 154.9 ppm; IR (KBr): $\tilde{\nu} = 2923$, 2853 (C−H), 1583, 1518 (C=N, ArC−C), 1255 cm^{-1} (C-O-C); MS (MALDI$^+$, dithranol): m/z: 4539.6 $[Ag_5pz_4]^+$, 3434.1 $[Ag_4pz_3]^+$, 2324.5 $[Ag_3pz_2]^+$, 2218.5 $[Ag_2pz_2]^+$, 2111.6 $[Agpz_2]^+$, 1109.8 $[Agpz]^+$, 1001.9 $[Hpz]^+$; elemental analysis calcd (%) for $C_{65}H_{111}AgN_2O_5$: C 70.4, H 10.1, N 2.5; found: C 70.2, H 9.95, N 2.6.

Compound $[Agpz^{3,3}]_n$: Yield: 67 %. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 0.85–0.91 (m, 18H), 1.25–1.51 (m, 84H), 1.64–1.69 (m, 12H), 3.60 (t, $J = 6.0$ Hz, 8H), 3.88 (t, $J = 5.6$ Hz, 4H), 6.72 (s, 1H), 6.87 ppm (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.1$, 22.7–32.0, 68.7, 73.4, 99.9, 103.5, 123.9, 126.0, 141.0, 153.6 ppm; IR (Nujol): $\tilde{\nu} = 1655$, 1487 (C=N, ArC−C), 1235, 1019 cm^{-1} (C-O-C); MS (MALDI$^+$, DCTB): m/z: 3902.0 $[Ag_4pz_3]^+$, 2637.3 $[Ag_3pz_2]^+$; elemental analysis calcd (%) for $C_{75}H_{131}AgN_2O_6$: C 71.2, H 10.4, N 2.2; found: C 71.5, H 10.5, N 2.2.

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