Decisive Influence of the Metal in Multifunctional Gold, Silver and Copper Metallacycles: High Quantum Yield Phosphorescence, Color Switching and Liquid Crystalline Behavior

Jorge Cored,[a†] Olga Crespo,[b] José Luis Serrano,[a,c] Anabel Elduque,[b] * and Raquel Giménez[a] *

[a] Instituto de Ciencia de Materiales de Aragón (ICMA), Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Zaragoza - CSIC, 50009 Zaragoza, Spain.

[b] Departamento de Química Inorgánica, Facultad de Ciencias, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Universidad de Zaragoza - CSIC, 50009 Zaragoza, Spain.

[c] Instituto de Nanociencia de Aragón (INA), Universidad de Zaragoza, 50018 Zaragoza, Spain.

[†] Present address: Instituto de Tecnología Química (ITQ), CSIC-Universitat Politècnica de València, 46022 Valencia, Spain

* Corresponding authors E-mail: anaelduq@unizar.es, rgimenez@unizar.es

Abstract: Three cyclic trinuclear pyrazolate complexes with Au(I), Ag(I) or Cu(I) have been studied. These complexes have interesting and distinct optical and thermal properties depending on the metal, namely liquid crystalline behavior, red or deep-red phosphorescence at room temperature, thermoluminochromism and response to silver ions. The selected ligand, 4-hexyl-3,5-dimethylpyrazolate, maximizes the effect that the nature of the metals has on the properties of the complexes, thus allowing the intermolecular metallophilic interactions to be responsible for the optical properties. Moreover, the gold and silver complexes show columnar liquid crystal phases at high temperature. All of the complexes have good solubility properties for processing as poly(methyl methacrylate) (PMMA) doped films. Films of the gold, silver and copper complexes show interesting optical behavior such as wide-range color switching or phosphorescence turn-on upon cooling. In addition, films of the gold complex show a bright color switching (red to blue) in the presence of silver ions. The gold and copper complexes are bright phosphors with phosphorescent quantum yields of 90% in PMMA films, the highest values reported for this class of compounds at room temperature.

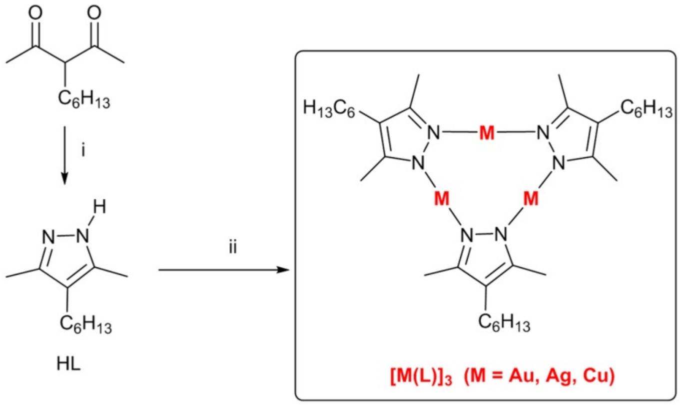
Introduction

Phosphorescent transition metal complexes build interest in quite diverse fields of materials science and life sciences. Important contributions for these complexes have been envisaged as luminescent materials in OLED displays and solid-state lighting technology,[1-3] or as stimuli-responsive materials with luminescent thermochromic or mechanochromic properties for memory, sensors or dosimeters, and bioimaging.[4-8]

Pyrazolate cyclic trinuclear complexes of the gold group $[M(pz^*)]_3$ (pz* = any pyrazolate derivative, M = Au, Ag, Cu) contain a nine-membered M_3N_6 metallacycle, and they are a special class of phosphorescent compounds. Since the first reports on the synthesis and structural characterization of such compounds,[9-12] a wide variety of supramolecular architectures have been described and these are modulated by intermolecular metallophilic interactions (attractive interactions between closed-shell metal centers) amongst other secondary interactions.[13, 14] In addition to the solid phase, and as another way to control the molecular aggregation, some complexes were reported to be liquid crystalline. These reports do not describe intermolecular metallophilic interactions. In this regard, the ligand design includes long aliphatic terminal chains that surround the metallacycle to drive the formation of such mesophases.[15-20]

More recently luminescent properties attributed to metal-metal interactions were discovered,[21] and this fostered the study of their optical and photophysical properties. Red emissions are predominant in solid phases at room temperature (RT), and emission energy dependence upon aggregation state, temperature and even excitation wavelength has been described.[13, 21-26] Mechanoluminochromism has also been reported for this class of complexes.[27] Emissive properties can also be influenced by other external factors such as the presence of organic vapors, ions or neutral molecules with basic or acidic character, which lead to the formation of adducts that in turn induce turn-on, quenching or emission color changes.[28-30] Applications as security inks,[31] and sensors based on smart gels,[24] or embedded in silica channels[30] have been envisaged. Studies on the luminescence of $[M(pz^*)]_3$ have mostly been focused on copper complexes,[27, 32-37] but there are fewer examples for gold[13, 38, 39] and hardly any for silver.[28, 34, 35] Very few luminescence studies on the three coinage metals are available for the same ligand and, as a consequence, the effect of the metal has hardly been studied.[21, 23]As far as quantum yields are concerned, high values have been found for complexes with trifluoromethyl-substituted pyrazolates but only at low temperatures $[M(3,5\text{-}(CF_3)_2Pz)]_3$ (98.8%, 87.7%, and 94.2% M = Cu, Ag, Au, at 4 K respectively);[23] and a RT value has recently been reported for M = Cu (82.2%).[40] Thus, quantum yield values at RT for a family of cyclic trinuclear $[MPz^*]_3$ complexes have not been fully described to date.

In the work reported here three analogous gold, silver and copper complexes $[M(L)]_3$ that are phosphorescent were studied (Scheme 1). It was found that the gold and copper complexes are bright red/deep-red phosphors at RT with exceptionally high quantum yields. The design of the ligand, 4-hexyl-3,5-dimethylpyrazolate, which bears only one short hexyl chain in the 4-position of the pyrazole ring, imparts good solubility properties for mixing with polymer matrices and film processing and it also induces liquid crystalline behavior. In addition, color switching occurs upon lowering the temperature. In order to better implement their sensor abilities, the responses of doped PMMA films to temperature or silver ions were also evaluated. The preparation of the three coinage metal complexes allowed a comparative study of the influence of the metal in terms of luminescence and thermal properties.



Scheme 1. Molecular structure of the trinuclear complexes studied in this work and synthetic route. i) semicarbazide hydrochloride, H_2O, reflux, 24h. ii) $[AuCl(S(CH_3)_2)]$, KOH, acetone, RT, 24h; or $AgPF_6$, NEt_3, acetone, RT, 24h; or $[Cu(CH_3CN)_4]BF_4$, NEt_3, acetone, RT, 24h.

Experimental section

Synthesis and characterization data

4-hexyl-3,5-dimethylpyrazole (HL). Semicarbazide hydrochloride (2.40 g, 22 mmol) was added to a suspension of 3-hexyl-2,4-pentanodione (4.06 g, 22 mmol) in distilled water (30 mL). Once the addition was complete, the mixture was heated to reflux and stirred for 24 h.

The reaction mixture was filtered and neutralized with sodium hydrogen carbonate until pH = 7 and then extracted with dichloromethane. Finally the organic layer was dried with $MgSO_4$ and the solvent was evaporated. The oily product was purified by flash column chromatography (hexane/ethyl acetate 9:1). It was obtained as a yellow oil that crystallized as a white solid over time or by cooling with liquid nitrogen. Yield: 45%. ^1H NMR (400 MHz, CD_2Cl_2, 20 ºC, TMS) δ = 7.92 (*br* s, 1H), 2.34 (t, J = 8.0 Hz, 2H), 2.18 (s, 6H), 1.44 (q, J = 8.0 Hz, 2H), 1.30 (m, 6H), 0.89 ppm (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2, 20 ºC, TMS) δ = 142.27, 116.29, 32.34, 31.25, 29.63, 23.49, 23.27, 14.44, 11.15 ppm. FTIR (KBr) v = 3201, 3150, 3091 (N-H), 2925, 2855 (C_{alq}-H), 1519 cm^{-1} (C=N, C_{ar}-C). HRMS (ESI^+, acetonitrile) *m/z* 181.1693 $[M+H]^+$ (calcd 181.1699).

Cyclo-tris(μ-(4-hexyl-3,5-dimethylpyrazolate)-N,N')-trigold(I) $[Au(L)]_3$. A solution of potassium pyrazolate prepared "*in situ*" by reaction of an acetone solution (11 mL) of **HL** (95.7 mg, 0.5 mmol) and KOH in methanol (2.1 mL, 0.5 mmol) was added dropwise to a suspension of $[AuCl\{S(CH_3)_2\}]$ (152.1 mg, 0.5 mmol) in acetone (12 mL). The reaction mixture was stirred for 24 h, at room temperature under an argon atmosphere and in the absence of light. Then, the solvent was evaporated to dryness. The addition of dichloromethane (20 mL) and filtration through Celite® led to a colourless solution. The solution was concentrated to ca. 1 mL. Methanol (10 mL) was added and the solid was separated by filtration, washed with methanol and vacuum-dried. White solid. Yield: 46%. ^1H NMR (400 MHz, CD_2Cl_2, 20 ºC, TMS) δ = 2.34 (t, J = 8.0 Hz, 6H), 2.17 (s, 18H), 1.43 (q, J = 8.0 Hz, 6H), 1.30 (m, 18H), 0.89 ppm (t, J = 8.0 Hz, 9H). ^{13}C NMR (100 MHz, CD_2Cl_2, 20 ºC, TMS) δ = 146.03, 116.14, 32.39, 31.49, 29.69, 24.63, 23.32, 14.47, 12.32 ppm. FTIR (KBr) v = 2956, 2921, 2850 (C_{alq}-H), 1514, 1487 cm^{-1} (C=N, C_{ar}-C). MS ($MALDI^+$, DCTB) *m/z* 1128.4 $[M]^+$. HRMS ($MALDI^+$, DCTB) *m/z* 1151.3399 $[M+Na]^+$ (calcd 1151.3539). Elemental analysis calcd (%) for $C_{33}H_{57}Au_3N_6$: C 35.11, H 5.09, N 7.45; found: C 35.01, H 4.83, N 7.28.

Cyclo-tris(μ-(4-hexyl-3,5-dimethylpyrazolate)-N,N')-trisilver(I) [Ag(L)]$_3$. A solution of triethylammonium pyrazolate prepared "*in situ*" by reaction of an acetone solution (8 mL) of **HL** (115.3 mg, 0.6 mmol) and triethylamine (93 µL, 0.7 mmol) was added dropwise to a solution of $AgPF_6$ (160.6 mg, 0.6 mmol) in acetone (12 mL). The reaction mixture was stirred for 22 h, at room temperature under an Argon atmosphere and in the absence of light. Then, the solvent was evaporated to dryness. The addition of dichloromethane (20 mL) and filtration through Celite® led to a colourless solution. The solution was concentrated to ca. 1 mL. Addition of methanol (10 mL) gave a solid, which was separated by filtration, washed with methanol and vacuum-dried. The compound was isolated as a white solid. Yield: 81%. ^{1}H NMR (400 MHz, CD_2Cl_2, 20 ºC, TMS) δ = 2.36 (t, J = 8.0 Hz, 6H), 2.07 (s, 18H), 1.44 (q, J = 8.0 Hz, 6H), 1.31 (m, 18H), 0.90 (t, J = 8.0 Hz, 9H). ^{13}C NMR (100 MHz, CD_2Cl_2, 20 ºC, TMS) δ = 147.67, 114.12, 32.42, 31.73, 29.75, 24.41, 23.35, 14.48, 12.95 ppm. FTIR (KBr) ν = 2954, 2924, 2850 (C_{alq}-H), 1504 cm^{-1} (C=N, C_{ar}-C). HRMS (MALDI^{+}, DCTB) *m/z* 965.0851 [M+Ag]$^{+}$ (calcd 965.0848). Elemental analysis calcd (%) for $C_{33}H_{57}Ag_3N_6$: C 46.01, H 6.67, N 9.76; found: C 45.85, H 6.59, N 9.67.

Cyclo-tris(μ-(4-hexyl-3,5-dimethylpyrazolate)-N,N')-tricopper(I) [Cu(L)]$_3$. A solution of triethylammonium pyrazolate prepared "in situ" by reaction of an acetone solution (9 mL) of HL (99.0 mg, 0.5 mmol) and triethylamine (77 µL, 0.6 mmol) was added dropwise to a solution of $[Cu(MeCN)_4]BF_4$ (172.8 mg, 0.5 mmol) in acetone (12 mL). The reaction mixture was stirred for 23 h, at room temperature under an Argon atmosphere and in the absence of light. Then, the solvent was evaporated to dryness. The addition of dichloromethane (20 mL) and filtration through Celite® led to a colourless solution. The solution is concentrated to ca. 1 mL. Addition of methanol (10 mL) gave a solid, which was separated by filtration, washed with methanol and vacuum-dried. The compound was isolated as a white solid. Yield: 82%. ^{1}H NMR (400 MHz, CD_2Cl_2, 20 ºC, TMS) δ = 2.37 (t, J = 8.0 Hz, 6H), 2.25 (s, 18H), 1.43 (q, J = 8.0 Hz, 6H), 1.30 (m, 18H), 0.89 ppm (t, J = 8.0 Hz, 9H). ^{13}C NMR (100 MHz, CD_2Cl_2, 20 ºC, TMS) δ = 147.67, 115.56, 32.40, 31.59, 29.71, 23.91, 23.31, 14.46, 12.87 ppm. FTIR (KBr) ν = 2954, 2922, 2851 (C_{alq}-H), 1508 cm^{-1} (C=N, C_{ar}-C). HRMS ($MALDI^+$, DCTB) *m/z* 726.2542 $[M]^+$ (calcd 726.2533) Elemental analysis calcd (%) for $C_{33}H_{57}Cu_3N_6$: C 54.41, H 7.89, N 11.54; found: C 54.18, H 7.77, N 11.48.

Film preparation

PMMA films of complexes at 5 wt% or 20 wt% were prepared by drop casting a solution of poly(methylmethacrylate) (19 or 16 mg, Mw =120000), complex (1 or 4 mg) and dichloromethane (0.5 mL) onto a substrate. Substrates were glass coverslips, for qualitative testing of the thermoluminochromic properties, or quartz coverslips for luminescent measurements. Films were dried under vacuum for 12 h. In order to prove reproducibility of the results three films were prepared for each complex. Quantum yield measurements were performed by triplicate using three different reference samples containing only PMMA.

Results and Discussion

Synthesis and characterization

4-Hexyl-3,5-dimethylpyrazole (**HL**) was prepared from 3-hexyl-2,4-pentanedione using hydrazine hydrate in ethanol as reported previously.[41] **HL** was also obtained by adapting a recent procedure for the synthesis of pyrazoles that uses semicarbazide hydrochloride in water as a sustainable alternative to avoid hydrazine derivatives.[42]

Metal complexes were synthesized by the procedure indicated in Scheme 1. Analytical and spectroscopic data are in accordance with the proposed structures. **HL** shows a broad NH signal at 11.1 ppm in the ^1H NMR spectrum in $CDCl_3$ or at 7.9 ppm in CD_2Cl_2, and three NH stretching vibrations at 3200, 3150 and 3091 cm^{-1} are present in the IR spectrum. As expected, these bands were not observed in the spectra of the metal complexes. The stoichiometry of the trinuclear complex was studied by mass spectrometry. The high tendency to fragmentation was minimized by using the MALDI-TOF technique and *trans*-2-(3-(4-tert-butylphenyl)-2-methyl-2-propenylidene)malononitrile (DCTB) as the matrix, with the $[M+Ag]^+$ signal obtained for the silver complex, and the molecular ion for the gold and copper complexes.

Thermal and liquid crystalline properties

Pyrazole ligand, **HL**, was obtained as a pale yellow oil from the synthesis, as reported previously. However, a white solid with a melting point of 46 °C could be obtained by freezing the oil with liquid nitrogen (Table 1).

Table 1. Thermogravimetric, DSC and XRD data.

Compound	$T_{5\%}$ / °C[a)]	T / °C (ΔH / kJ mol^{-1})[b)]
HL	135	Cr 46 (22.4) I
$[Au(L)]_3$	271	Cr 118 (17.8) Cr' 140[c)] Col 143[c)] Col' 145[c)] (14.9)[d)] I[e)]
$[Ag(L)]_3$	296	Cr 126 (3.1) Cr' 186 (11.2) Col$_r$ 193 (3.2) I[e)]
$[Cu(L)]_3$	335	Cr 116 (38.7) I

Cr: crystal phase, Col: unknown columnar mesophase, Col$_r$: rectangular columnar mesophase I: isotropic liquid. [a)] Temperature corresponding to 5% weight loss by thermogravimetric analysis at a rate of 10 °C min^{-1}. [b)] DSC data for the first heating cycle at a rate of 10 °C min^{-1} and onset temperatures. [c)] POM data. [d)] Combined enthalpy. [e)] Partial decomposition in the isotropic liquid.

Metal complexes were obtained as white solids and these showed different thermal behavior (Table 1). Thermogravimetric analysis of the trinuclear complexes show that they are stable towards volatile decomposition up to temperatures as high as 270 °C (Figure S1), and the order of stability is Cu > Ag > Au. However, differential scanning calorimetry (DSC) showed that the gold and silver complexes decompose at temperatures close to the isotropic liquid without volatile formation, with non-reproducible heating/cooling cycles observed if the sample reached the isotropic liquid temperature. Metal deposits were clearly observed by polarized optical microscopy (POM) in the isotropic liquid for the silver analog. This silver complex was recently described as a novel precursor for the *in situ* deposition of metallic silver onto mechanical surfaces with applications as high performance lubricants. However, although a clean thermolysis at high temperatures was reported, the liquid crystalline properties of this complex were not studied.[43]

A study by polarizing optical microscopy (POM) and DSC (Figures 1 and S2) showed that the gold and silver complexes are columnar liquid crystals at high temperature.[44, 45] When analyzing the samples, particular care was taken not to heat the material to the liquid phase in an effort to avoid decomposition and obtain reproducible results. **[Au(L)]$_3$** displayed mesomorphism both on heating and cooling. On heating two mesophases appeared whose textural changes were more evident at POM in the first cooling cycle (Figures 1a-b). At 145 ºC a dendritic texture with homeotropic (black) domains developed and this was followed at 143 ºC by a texture in which the homeotropic areas were lost and a broken texture was observed. Then, another change, not as sharp as the previous one, occurred at around 140-137 ºC giving a smoother texture (Figure 1c). Unfortunately, DSC thermograms did not shed light about this behavior. Only one peak was observed at those temperatures even at low scan rates (Figures 1d and S2). On further cooling a sharp textural change occurred at 121 °C to give a crystal phase different from the initial one. X-ray diffraction studies at different temperatures were carried out but the samples decomposed during the experiments due to a combined effect of temperature and exposure to X-ray radiation. As a consequence, indexation was not possible. The results of the experiments outlined above tentatively allow us to rule out the hexagonal symmetry for the lower temperature mesophase. **[Ag(L)]$_3$** melts at a higher temperature than the gold analog and it exhibits a fluid liquid crystal phase between 186 °C and 193 °C. The texture of this phase is consistent with a columnar mesophase (Figure 1e). The X-ray diffractogram contained a set of reflections that could be indexed to a rectangular columnar mesophase (lattice parameters a = 22.3 Å, b = 24.5 Å) (Figure S3). **[Cu(L)]$_3$** is not liquid crystalline but melts to an isotropic liquid at 116 °C, i.e., at a lower temperature than the gold and silver complexes, which is advantageous for thermal processing.

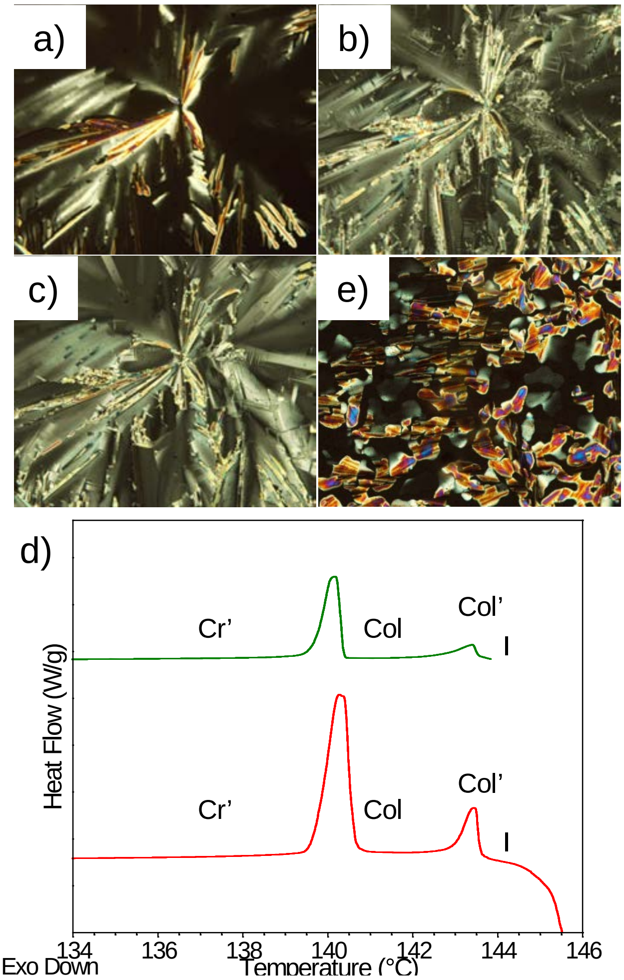


Figure 1. POM microphotographs (crossed polarizers) of the texture changes that occur in the same sample area on cooling the isotropic liquid for **[Au(L)]$_3$**: a) 145 °C, b) 142 °C, c) 139 °C. d) First DSC heating cycle for **[Au(L)]$_3$** at a rate of 2 ºC min^{-1} (red line) or 1 ºC min^{-1} (green line). e) POM microphotograph (crossed polarizers) of the texture shown by **[Ag(L)]$_3$** at 191 °C.

By comparing the thermal behavior of the three complexes it can be observed that the transition temperatures to the isotropic liquid decrease in the order Ag > Au > Cu. This trend means that there are stronger intermolecular interactions for the silver complex. In fact, in the crystal structure of **[Ag(L)]$_3$**,[43] stacked molecules forming chains with intermolecular Ag…Ag distances as short as 3.17 Ǻ are observed. They are shorter than 3.44 Ǻ, which is the sum of the van der Waals radii of two silver atoms, and this makes evident the presence of metallophilicity. Failing structural data to compare the three complexes, a support to the trend observed here are the reported single crystal structures of isostructural gold, silver and copper $[M(3,5\text{-}(CF_3)_2Pz)]_3$ complexes.[23] There it is shown that intermolecular M…M distances are shorter for the silver complex than for the gold and copper ones. But metallophilic bonds are known to enlarge with temperature due to their soft character,[23] and they are only one component among other intermolecular forces that could control the mesophase formation, i.e. the strength of M-L bonds influencing the aromaticity of the pyrazolate rings,[46] and therefore π-stacking interactions, and London forces due to the alkyl groups.

However, it is rare to obtain columnar mesomorphism from C_3 symmetric molecules with such a low number of short aliphatic chains (only three hexyl chains),[45, 47-49] and the behavior observed represent an improvement on the previously reported properties for gold complexes with longer chains, for which monotropic (thermodynamically unstable) mesophases were described.[17] With such a low number of alkyl chains directly attached to the pyrazolate ring, we observe that columnar liquid crystal behavior is distinctively influenced by the metal,[50] the most stable mesophase showed by the silver complex, with the metals facilitating the shortest metallophilic interactions.

Luminescent properties and color switching

The group 11 metals in the three macrocycles not only influence their mesogenic properties but also the key in the luminescent behavior. Whereas in dilute solutions all complexes show emission bands at around 340-350 nm, i.e., similar to the emission band of the pyrazole ligand **HL** (Figure S4), they behave differently in the solid state (Table 2). As mentioned above, **HL** could be crystallized and studied in powder form and a very weak structured emission band was observed, which was only evident in thin powder samples at RT. A broad, more intense, band was also observed at lower energy at around 480 nm at RT and 508 nm at 77 K. The maximum of this broad band changes slightly with the excitation maximum. (Figure S5).

Table 2. Emission data of the complexes as neat powder samples.

Compound	$\lambda_{emission}$ / nm		τ / µs [*R-Square*]	
	RT	77 K	RT	77 K
HL	480a)	508a)	34 [1.116]b),c)	5556 [0.955]c),d)
[Au(L)]$_3$	709	373e	13.5 [1.04]f)	169 [0.969]f)
[Ag(L)]$_3$	-	448	-	138.1 [0.997]g)
[Cu(L)]$_3$	631	644	42.8 [0.998]g)	64.7 [0.999]g)

a) Maximum corresponding to a broad band. b) Lifetime measured at $\lambda_{excitation}$ = 370 nm. c) Average lifetime <τ> from data fitted to a double exponential, data at room temperature: a_1 = 943.3, τ_1 = 2.36 µs , a_2 = 978.7, τ_2 = 35,6 µs; at 77K: $a_1 = 3.05\ 10^7$, τ_1 = 48 µs, $a_2 = 1,114\ 10^6$, τ_2 = 6644 µs . d) Lifetime measured at $\lambda_{excitation}$ = 400 nm. e) Highest intensity peak of the structured emission band. f) Lifetime measured at $\lambda_{excitation}$ = 254 nm. g) Lifetime measured at $\lambda_{excitation}$ = 295 nm

Different emissive behavior was observed for the [M(L)]$_3$ complexes, depending on the metal. Powder samples of the gold complex had a red glow at RT. The luminescence spectrum contains a broad band at 709 nm and a lifetime of 13.5 microseconds was measured at that wavelength. This finding is consistent with the low energy (LE) emission bands previously observed for crystal samples of other gold pyrazolate complexes at RT, which were proposed to be originated from centered excimeric (^{3}MM) states due to intertrimer aurophilic interactions.[13, 23] Emissions in the orange-red region have also been reported for gold pyrazolate complexes as dendron fibers or gels at RT.[21, 24] In contrast, at 77 K a structured emission with a longer lifetime was observed and the most intense peak was observed at 373 nm, thus yielding a blue color emission (Figure 2a). This finding indicates that the emitting state has a different origin from that at RT. The average spacing between the structured peaks is around 1400 cm^{-1}, which corresponds well with the pyrazolate ring vibrations,[51] and resembles the spacing found in the emissions of other pyrazole ligands and pyrazolate complexes. This emission is assigned to ligand-centered phosphorescence sensitized via the internal heavy atom effect[25, 52 53] or delayed fluorescence.[27] The study of our compounds in solution also fit with this point. Crystalline samples of $[Au(3,5-(CF_3)_2Pz)]_3$ show thermochromism from red to blue upon cooling,[23] but in this case the blue color was not a structured emission and it was explained as being consequence of the emission from different ^{3}MM excimer emitting states.

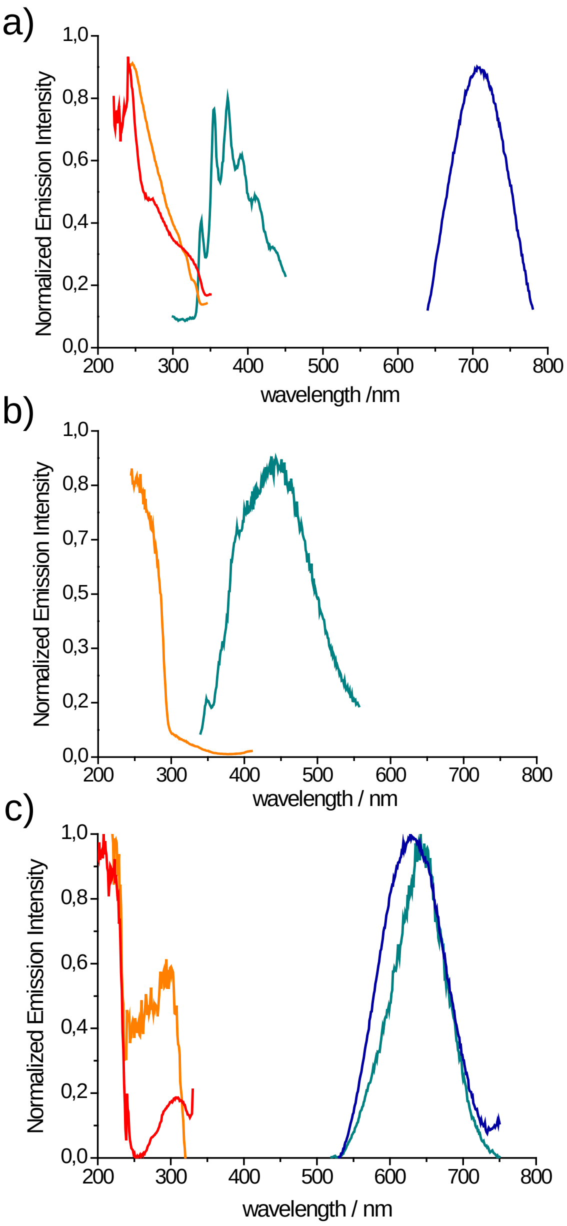


Figure 2. Powder samples. Excitation spectra at RT (red line), and at 77 K (orange line) Emission spectra at RT (dark blue line) and 77 K (blue-green line) for a) **[Au(L)]$_3$**, b) **[Ag(L)]$_3$**, c) **[Cu(L)]$_3$**.

In contrast, the silver complex in powder form is not luminescent at RT, but glows blue at low temperature (Figure 2b), with a lifetime of 138 μs at 77 K. The band is observed in the same region as that described for the free ligand, albeit with a shorter lifetime. Very few comparisons can be made in this respect, as silver trinuclear pyrazolates have only rarely been analyzed. The emission observed resembles the broad band reported for $[Ag(3,5\text{-}(CF_3)_2Pz)]_3$ at 77 K (also attributed to ^{3}AgAg excimers (τ = 38 μs)).[23] However, the emission band also shows some vibronic progression at the higher energy side, in a similar way to the gold complex, and this points to overlap with a ligand-centered emission.

Powder samples of the copper complex display a red emission at RT and 77 K with a slight decrease in the emission energy and increase in the lifetime upon cooling (Table 2), i.e., a temperature change barely affected the emission (Figure 2c). As mentioned above, copper species are the most widely studied among cyclic trinuclear pyrazolate complexes. Red emissions are generally observed at RT for these species, but although red-orange emissions are also observed at low temperature, yellow, green or even blue emissions have been also reported at low temperature.[24, 25] Phosphorescence originating from an excited ^{3}MM state is proposed to explain these emissions, as in the gold complexes.

In summary, **$[Au(L)]_3$** shows luminescence thermochromism on cooling. Gold and copper complexes show red emissions at RT upon excitation at 254 nm with large lifetimes in accordance with a phosphorescent emission. The large Stokes' shifts observed are consistent with significant excited-state distortions for these materials.[54]

The complexes were dispersed in PMMA at 5 wt% and processed as thin films in order to take advantage of their luminescent properties for testing applications (Figure 3 and Video S1, S2 and S3). PMMA doped films of the gold and copper complexes display red emissions with a very high quantum yield at RT (QY = 0.9). Although these values are comparable to those reported for complexes $[M(3,5\text{-}(CF_3)_2Pz)]_3$ [M = Cu, Ag, Au], to our knowledge they represent the highest values reported for homometallic complexes of formula $[M(Pz)]_3$ at RT.[23, 40] The red color observed at RT for the gold complex was different from the one shown by the copper complex, as shown in the CIE 1931 chromaticity coordinates obtained from the emission spectrum after removing excitation light, which gave values of X = 0.59, Y = 0.31 for the gold compound and X = 0.61, Y = 0.36 for the copper one (Figure S6). PMMA films of the silver complex are not luminescent at RT, but on cooling they show a luminescence turn-on and emit blue light (Figure 3b). This behavior is analogous to that in the powder state.

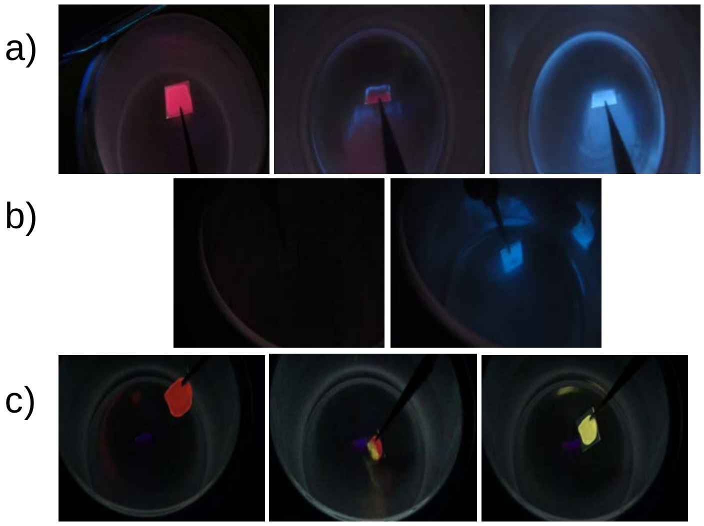


Figure 3. Video snapshots of the luminescence color switching of PMMA films (5 wt%) (λ_{exc} = 254 nm), from RT (left) to 77 K (right) for a) **$[Au(L)]_3$**, b) **$[Ag(L)]_3$**, c) **$[Cu(L)]_3$**. (See Video S1, S2 and S3)

Interestingly, the 5 wt% PMMA films of the gold and copper complexes show fast and bright luminescence color switching on cooling to 77 K. The gold complex changes from red to blue (Figure 3a) and the copper complex changes from red to yellow (Figure 3c). The emission spectra of these films were studied at different temperatures (Figure 4). Films of **$[Au(L)]_3$** at RT show an emission band corresponding to the observed red color at 736 nm, and this red emission is present in the temperature range 298 to ca. 180 K. However, as the temperature decreases from 180 to 77 K a high energy band corresponding to the blue emission appears.

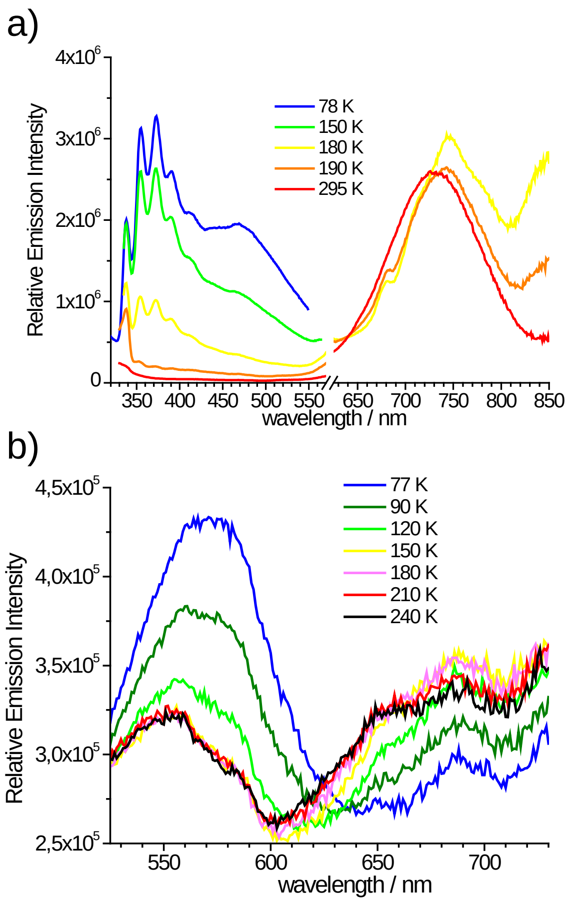


Figure 4. Temperature dependence of the emissive behavior of PMMA films (5 wt%) a) **$[Au(L)]_3$** at λ_{exc} = 295 nm, b) **$[Cu(L)]_3$**. at λ_{exc} = 248 nm.

The film of **$[Cu(L)]_3$** displays dual emission in the red and yellow-green regions in the 240-77 K range. At low temperature the yellow-green band is dominant, whereas at higher temperatures the red component is the most relevant. As a result different intermediate colors can be observed by the human eye depending on the temperature. The lifetimes of both components are very similar and they became shorter as the temperature was increased (Tables S1 and S2). These results are consistent with those described for other thermoluminochromic copper complexes.[25] Depopulation of the higher-energy emitting states upon heating may take place. As a result of thermal relaxation between different ^{3}MM excimer emitting states, different relative intensities for the dual emission are observed.

As a general trend, for both complexes and increase in the lifetime for the same emissive state on decreasing the temperature have been observed, as in other trinuclear cyclic pyrazolates[23, 25] and this is expected as an increase in the temperature increment should increase the efficiency of nonradiative pathways (Table S1). In addition, an increase in the lifetime for films is observed when compared to those of powder samples. The data indicate that quenching processes are diminished in films, although the specific processes are difficult to elucidate. The fact that the copper complex at 77 K shows yellow luminescence in PMMA films and red luminescence in solid powder is remarkable and indicates a higher sensitivity to the environment of the copper complex compared to the analogous gold complex.

In order to extract further information, PMMA films of gold and copper complexes were also tested at a higher concentration (20 wt%). Qualitatively they showed the same colors than the 5 wt% films at RT and 77 K (Figure S7). In addition, luminescence spectra on cooling were recorded (Figure S8). For the gold complex two bands (blue and red) were observed, and no relevant change in the temperature at which the red component becames more important (ca 180K) was observed compared with 5 wt% films. Thus, concentration seems not to affect to the thermoluminescent behavior of the gold complex.

However, the copper complex emission changed from red (RT) to yellow-orange (77 K), as in the 5 wt% films, but the two bands (yellow and red component) overlap. The red component is more important at low temperature than for the 5 wt% films, and T ca. 159 K only the red emission was observed. Interestingly, as the PMMA quantity increases from the pure solid (in which the yellow component at 77 K is not observed) to the 5 wt% films (in which the yellow component is observed at any temperature from 77 K to 298 K) the yellow component exists in a wider range of temperature, the red and yellow bands overlap less, and the temperature at which the red component became the most important decreases (ca. 159 K for 20 wt% and ca. 120 K for 5 wt%).

The obtained results indicate that the color switching behavior of copper complex is sensitive to both temperature and concentration in the PMMA matrix.

Finally, it has been reported that cyclic trinuclear gold complexes can interact with silver ions due to the formation of Au_3-Ag-Au_3 sandwich clusters with Au-Au and Au-Ag interactions,[55, 56] and this leads to luminescent complexes. For the particular case of pyrazolate trinuclear complexes, luminescence changes have been observed upon the addition of a silver salt to the trinuclear gold complex in the gel state,[24] confined in nanochannels[30] nanoaggregates in solution or powder samples[57] and more recently in aqueous media.[58] Here we demonstrate behavior without precedent, in that a luminescence color switch with high contrast takes place by simply dipping a PMMA film of the gold complex in a silver nitrate solution. Red luminescent films of the gold complex change to a turquoise color at RT when they are in contact with the silver nitrate solution (Figure 5 and Video S4). The emission spectrum of the exposed film shows a band with a maximum at 495 nm.

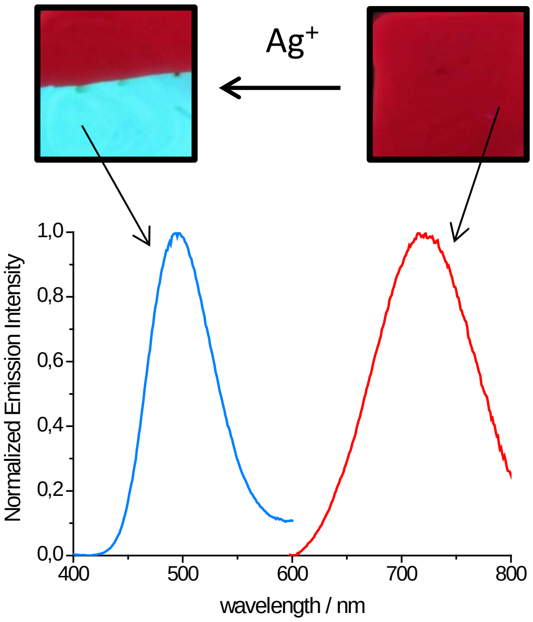


Figure 5. Emission spectra (λ_{exc} = 295 nm) and photographs of a PMMA film (λ_{exc} = 254 nm) of **$[Au(L)]_3$** before and after dipping the lower half on a silver nitrate solution in methanol. See also Video S4.

Conclusion

Metal-containing (Au, Ag and Cu) cyclic trinuclear complexes derived from 4-hexyl-3,5-dimethylpyrazolate show interesting thermal, luminescent and solubility properties for functional materials. Liquid crystalline behavior, efficient phosphorescence, thermoluminochromism and ionic response have been found. The presence of the hexyl tails allows the observation of isotropization temperatures and columnar liquid crystal behavior for gold and silver complexes. In addition, this ligand maximizes the effect that the metal has on the mesomorphic and luminescent properties, which are affected by metallophilic interactions. In relation to luminescent properties, in powder form the silver complex is only luminescent at low temperature, whereas the gold and copper complexes are red phosphors at RT.

All of the complexes have good solubility properties. This allows easy solution processing as thin films in a PMMA matrix. Films of gold and copper complexes show phosphorescent quantum yields of 90% at RT, the highest values reported for this class of complexes at RT. Films of the gold complex display thermoluminochromism and ionoluminochromism with a remarkable color change (from red to blue), the silver complex shows a phosphorescence turn-on, and the copper complex exhibits a gradual emission color change upon cooling (from red to yellow). This color change upon cooling is also sensitive to the amount of compound in the polymer matrix.

In conclusion, the nature of the group 11 metals represents the key in the emissive properties of these complexes from which the copper and gold species have proven to be highly efficient red/deep-red phosphors at RT with sensor abilities and the prospect of technological applications.

Acknowledgements

This work was supported by MINECO-FEDER, UE (projects MAT2015-66208-C3-1-P, CTQ2015-70174-P, CTQ2014-53033-P, CTQ2016-75816C2-1-P), Gobierno de Aragón-FSE, UE, and Cátedra IQE (Industrias Químicas del Ebro) for a postgraduated grant (J. C.). Authors thank Joaquín Barberá for XRD experiments and helpful discussions, and the use of Servicios Científico-Técnicos of CEQMA (UZ-CSIC).

Supporting Information description

Materials and methods. Figures S1-S8. Tables S1 and S2 (PDF). Video files S1-S4 (AVI).

References

1. Tang, M. C.; Chan, A. K. W.; Chan, M. Y.; Yam, V. W. W. Platinum and Gold Complexes for OLEDs. In *Topics Curr. Chem.* **2016**; Vol. 374.

2. Yam, V. W.-W.; Au, V. K.-M.; Leung, S. Y.-L. Light-Emitting Self-Assembled Materials Based on d^8 and d^{10} Transition Metal Complexes. *Chem. Rev.* **2015**, *115*, 7589-7728.

3. Li, Z. R. *Organic Light-Emitting Materials and Devices*. CRC Press: Boca Raton, 2015.

4. Sagara, Y.; Yamane, S.; Mitani, M.; Weder, C.; Kato, T. Mechanoresponsive Luminescent Molecular Assemblies: An Emerging Class of Materials. *Adv. Mater.* **2016**, *28*, 1073-1095.

5. Zhang, X.; Chi, Z.; Zhang, Y.; Liu, S.; Xu, J. Recent advances in mechanochromic luminescent metal complexes. *J. Mater. Chem. C* **2013**, *1*, 3376-3390.

6. Sagara, Y.; Kato, T. Mechanically induced luminescence changes in molecular assemblies. *Nat. Chem.* **2009**, *1*, 605-610.

7. Zhao, Q.; Li, F.; Huang, C. Phosphorescent chemosensors based on heavy-metal complexes. *Chem. Soc. Rev.* **2010**, *39*, 3007-30.

8. Abdou, H. E.; Mohamed, A. A.; Fackler, J. P.; Burini, A.; Galassi, R.; López-de-Luzuriaga, J. M.; Olmos, M. E. Structures and properties of gold(I) complexes of interest in biochemical applications. *Coord. Chem. Rev.* **2009**, *253*, 1661-1669.

9. Bonati, F.; Minghetti, G.; Banditelli, G. Trimeric gold(I) derivatives of pyrazoles: a novel type of inorganic ring. *Chem. Commun.* **1974**, 88-89.

10. Murray, H. H.; Raptis, R. G.; Fackler, J. P. Syntheses and X-Ray Structures of Group-11 Pyrazole and Pyrazolate Complexes - X-Ray Crystal-Structures of Bis(3,5-Diphenylpyrazole)Copper(II) Dibromide, Tris(μ-3,5-Diphenylpyrazolato-N,N')Trisilver(I)-2-Tetrahydrofuran, Tris(μ-3,5-Diphenylpyrazolato-N,N')Trigold(I), and Hexakis(μ-3,5-Diphenylpyrazolato-N,N')Hexagold(I). *Inorg. Chem.* **1988**, *27*, 26-33.

11. Raptis, R. G.; Fackler, J. P. Structure of Tris(μ-3,5-Diphenylpyrazolato-N,N')Tricopper(I) - Structural Comparisons with Silver(I) and Gold(I) Pyrazolate Trimers. *Inorg. Chem.* **1988**, *27*, 4179-4182.

12. Ehlert, M. K.; Rettig, S. J.; Storr, A.; Thompson, R. C.; Trotter, J. Synthesis and X-Ray Crystal-Structure of the 3,5-Dimethylpyrazolato Copper(I) Trimer, [Cu(Pz")]$_3$. *Can. J. Chem.* **1990**, *68*, 1444-1449.

13. Yang, G.; Raptis, R. G. Supramolecular assembly of trimeric gold(I) pyrazolates through aurophilic attractions. *Inorg. Chem.* **2003**, *42*, 261-263.

14. Burini, A.; Mohamed, A. A.; Fackler, J. P. Cyclic trinuclear gold(I)compounds: Synthesis, structures and supramolecular acid-base pi-stacks. *Comments Inorg. Chem.* **2003**, *24*, 253-280.

15. Barberá, J.; Elduque, A.; Giménez, R.; Oro, L. A.; Serrano, J. L. Pyrazolate "golden" rings: Trinuclear complexes that form columnar mesophases at room temperature. *Angew. Chem. Int. Ed.* **1996**, *35*, 2832-2835.

16. Barberá, J.; Elduque, A.; Giménez, R.; Lahoz, F. J.; López, J. A.; Oro, L. A.; Serrano, J. L. (Pyrazolato)gold complexes showing room-temperature columnar mesophases. Synthesis, properties, and structural characterization. *Inorg. Chem.* **1998**, *37*, 2960-2967.

17. Kim, S. J.; Kang, S. H.; Park, K.-M.; Kim, H.; Zin, W.-C.; Choi, M.-G.; Kim, K. Trinuclear Gold(I) Pyrazolate Complexes Exhibiting Hexagonal Columnar Mesophases with Only Three Side Chains. *Chem. Mater.* **1998**, *10*, 1889-1893.

18. Torralba, M. C.; Ovejero, P.; Mayoral, M. J.; Cano, M.; Campo, J. A.; Heras, J. V.; Pinilla, E.; Torres, M. R. Silver and gold trinuclear complexes based on 3-substituted or 3,5-disubstituted pyrazolato ligands. X-ray crystal structure of cyclo-tris{μ-[3,5-bis(4-phenoxyphenyl)-1H-pyrazolato-κ N-1 :κ N-2]}trigold dichloromethane ([Au(μ-pz(pp2))](3) center dot CH_2Cl_2). *Helv. Chim. Acta* **2004**, *87*, 250-263.

19. Barberá, J.; Lantero, I.; Moyano, S.; Serrano, J. L.; Elduque, A.; Giménez, R. Silver Pyrazolates as Coordination-Polymer Luminescent Metallomesogens. *Chem. Eur. J.* **2010**, *16*, 14545-14553.

20. Beltrán, E.; Barberá, J.; Serrano, J. L.; Elduque, A.; Giménez, R. Chiral cyclic trinuclear gold(I) complexes with a helical columnar phase. *Eur. J. Inorg. Chem.* **2014**, 1165-1173.

21. Enomoto, M.; Kishimura, A.; Aida, T. Coordination metallacycles of an achiral dendron self-assemble via metal-metal interaction to form luminescent superhelical fibers. *J. Am. Chem. Soc.* **2001**, *123*, 5608-5609.

22. Dias, H. V. R.; Diyabalanage, H. V. K.; Rawashdeh-Omary, M. A.; Franzman, M. A.; Omary, M. A. Bright Phosphorescence of a Trinuclear Copper(I) Complex: Luminescence Thermochromism, Solvatochromism, and “Concentration Luminochromism”. *J. Am. Chem. Soc.* **2003**, *125*, 12072-12073.

23. Omary, M. A.; Rawashdeh-Omary, M. A.; Gonser, M. W. A.; Elbjeirami, O.; Grimes, T.; Cundari, T. R. Metal effect an the supramolecular structure, photophysics, and acid-base character of trinuclear pyrazolato coinage metal complexes. *Inorg. Chem.* **2005**, *44*, 8200-8210.

24. Kishimura, A.; Yamashita, T.; Aida, T. Phosphorescent Organogels via “Metallophilic” Interactions for Reversible RGB−Color Switching. *J. Am. Chem. Soc.* **2005**, *127*, 179-183.

25. Dias, H. V. R.; Diyabalanage, H. V. K.; Eldabaja, M. G.; Elbjeirami, O.; Rawashdeh-Omary, M. A.; Omary, M. A. Brightly Phosphorescent Trinuclear Copper(I) Complexes of Pyrazolates: Substituent Effects on the Supramolecular Structure and Photophysics. *J. Am. Chem. Soc.* **2005**, **127**, 7489-7501.

26. Lintang, H. O.; Kinbara, K.; Tanaka, K.; Yamashita, T.; Aida, T. Self-Repair of a One-Dimensional Molecular Assembly in Mesoporous Silica by a Nanoscopic Template Effect. *Angew. Chem. Int. Ed.* **2010**, *122*, 4337-4341.

27. Xiao, Q.; Zheng, J.; Li, M.; Zhan, S.-Z.; Wang, J.-H.; Li, D. Mechanically Triggered Fluorescence/Phosphorescence Switching in the Excimers of Planar Trinuclear Copper(I) Pyrazolate Complexes. *Inorg. Chem.* **2014**, *53*, 11604-11615.
28. Rawashdeh-Omary, M. A.; Rashdan, M. D.; Dharanipathi, S.; Elbjeirami, O.; Ramesh, P.; Dias, H. V. R. On/off luminescence vapochromic selective sensing of benzene and its methylated derivatives by a trinuclear silver(i) pyrazolate sensor. *Chem. Commun.* **2011**, *47*, 1160-1162.
29. Rawashdeh-Omary, M. A. Remarkable Alteration of Photophysical Properties of Cyclic Trinuclear Complexes of Monovalent Coinage Metals upon Interactions with Small Organic Molecules. *Comments Inorg. Chem.* **2013**, *33*, 88-101.
30. Lintang, H. O.; Kinbara, K.; Yamashita, T.; Aida, T. Metal-Ion Permeation in Congested Nanochannels: The Exposure Effect of Ag^+ Ions on the Phosphorescent Properties of a Gold(I)-Pyrazolate Complex that is Confined in the Nanoscopic Channels of Mesoporous Silica. *Chem. Asian J.* **2012**, *7*, 2068-2072.
31. Kishimura, A.; Yamashita, T.; Yamaguchi, K.; Aida, T. Rewritable phosphorescent paper by the control of competing kinetic and thermodynamic self-assembling events. *Nat. Mater.* **2005**, *4*, 546-549.
32. Gong, F.; Wang, Q.; Chen, J.; Yang, Z.; Liu, M.; Li, S.; Yang, G.; Bai, L.; Liu, J.; Dong, Y. Exploring Intertrimer Cu···Cu Interactions and Further Phosphorescent Properties of Aryl Trimer Copper(I) Pyrazolates via Substituent Changing and External Pressure. *Inorg. Chem.* **2010**, *49*, 1658-1666.
33. Gao, G.-F.; Li, M.; Zhan, S.-Z.; Lv, Z.; Chen, G.-h.; Li, D. Confined Metallophilicity within a Coordination Prism. *Chem. Eur. J.* **2011**, *17*, 4113-4117.
34. Jozak, T.; Sun, Y.; Schmitt, Y.; Lebedkin, S.; Kappes, M.; Gerhards, M.; Thiel, W. R. New Hexanuclear Group 11 Pyrazolate Complexes: Synthesis and Photophysical Features. *Chem. Eur. J.* **2011**, *17*, 3384-3389.
35. Hettiarachchi, C. V.; Rawashdeh-Omary, M. A.; Korir, D.; Kohistani, J.; Yousufuddin, M.; Dias, H. V. R. Trinuclear Copper(I) and Silver(I) Adducts of 4-Chloro-3,5-bis(trifluoromethyl)pyrazolate and 4-Bromo-3,5-bis(trifluoromethyl)pyrazolate. *Inorg Chem* **2013**, *52*, 13576-13583.
36. Wang, X.-L.; Zheng, J.; Li, M.; Weng Ng, S.; Chan, S. L.-F.; Li, D. Curved Cyclic Trimers: Orthogonal Cu–Cu Interaction versus Tetrameric Halogen Bonding. *Cryst. Growth Des.* **2016**, *16*, 4991-4998.
37. Cariati, E.; Lucenti, E.; Botta, C.; Giovanella, U.; Marinotto, D.; Righetto, S. Cu(I) hybrid inorganic–organic materials with intriguing stimuli responsive and optoelectronic properties. *Coord. Chem. Rev.* **2016**, *306*, 566-614.
38. Earl, L. D.; Nagle, J. K.; Wolf, M. O. Tuning the Extended Structure and Electronic Properties of Gold(I) Thienyl Pyrazolates. *Inorg. Chem.* **2014**, *53*, 7106-7117.
39. Ni, W.-X.; Li, M.; Zheng, J.; Zhan, S.-Z.; Qiu, Y.-M.; Ng, S. W.; Li, D. Approaching White-Light Emission from a Phosphorescent Trinuclear Gold(I) Cluster by Modulating Its Aggregation Behavior. *Angew. Chem. Int. Ed.* **2013**, *52*, 13472-13476.
40. Galassi, R.; Ghimire, M. M.; Otten, B. M.; Ricci, S.; McDougald, R. N.; Almotawa, R. M.; Alhmoud, D.; Ivy, J. F.; Rawashdeh, A.-M. M.; Nesterov, V. N.; Reinheimer, E. W.; Daniels, L. M.; Burini, A.; Omary, M. A. Cupriphication of gold to sensitize metal–metal bonds and near-unity phosphorescence quantum yields. *PNAS* **2017**, *114*, E5042.
41. Koóš, M.; Steiner, B.; Repáš, M. Influence of structure on antimicrobial activity of some heterocycles. 1. Alkylpyrazoles and alkylisoxazoles. *Chem. Papers* **1991**, *45*, 279-286.
42. Marković, V.; Joksović, M. D., "On water" synthesis of N-unsubstituted pyrazoles: semicarbazide hydrochloride as an alternative to hydrazine for preparation of pyrazole-3-carboxylate derivatives and 3,5-disubstituted pyrazoles. *Green Chem.* **2015**, *17*, 842-847.

43. Desanker, M.; Johnson, B.; Seyam, A. M.; Chung, Y.-W.; Bazzi, H. S.; Delferro, M.; Marks, T. J.; Wang, Q. J. Oil-Soluble Silver–Organic Molecule for in Situ Deposition of Lubricious Metallic Silver at High Temperatures. *ACS Appl. Mater. Interfaces* **2016**, *8*, 13637-13645.

44. Kumar, S. *Chemistry of Discotic Liquid Crystals*. Taylor & Francis: Boca Raton, 2011.

45. Wöhrle, T.; Wurzbach, I.; Kirres, J.; Kostidou, A.; Kapernaum, N.; Litterscheidt, J.; Haenle, J. C.; Staffeld, P.; Baro, A.; Giesselmann, F.; Laschat, S. Discotic Liquid Crystals. *Chem. Rev.* **2016,** *116*, 1139-1241.

46. Caramori, G. F.; Piccoli, R. M.; Segala, M.; Munoz-Castro, A.; Guajardo-Maturana, R.; Andrada, D. M.; Frenking, G. Cyclic trinuclear copper(I), silver(I), and gold(I) complexes: a theoretical insight. *Dalton Trans.* **2015**, *44*, 377-385.

47. Laschat, S.; Baro, A.; Steinke, N.; Giesselmann, F.; Hagele, C.; Scalia, G.; Judele, R.; Kapatsina, E.; Sauer, S.; Schreivogel, A.; Tosoni, M. Discotic liquid crystals: From tailor-made synthesis to plastic electronics. *Angew. Chem. Int. Ed.* **2007**, *46*, 4832-4887.

48. Heiney, P. A., Heiney, P. A. Structure and Physical Properties of Columnar Liquid Crystals. In Handbook of Liquid Crystals (eds J. W. Goodby, C. Tschierske, P. Raynes, H. Gleeson, T. Kato and P. J. Collings), 2014.

49. Wang, Y.; Shi, J.; Chen, J.; Zhu, W.; Baranoff, E. Recent progress in luminescent liquid crystal materials: design, properties and application for linearly polarised emission. *J. Mater. Chem. C* **2015**, *3*, 7993-8005.

50. Krikorian, M.; Liu, S.; Swager, T. M. Columnar Liquid Crystallinity and Mechanochromism in Cationic Platinum(II) Complexes. *J. Am. Chem. Soc.* **2014**, *136*, 2952-2955.

51. King, S. T. Low-Temperature Matrix Isolation Study of Hydrogen-Bonded, High-Boiling Organic Compounds. I. The Sampling Device and the Infrared Spectra of Pyrazole, Imidazole, and Dimethyl Phosphinic Acid. *J. Phys. Chem.* **1970**, *74*, 2133-2138.

52. Ovejero, P.; Mayoral, M. J.; Cano, M.; Lagunas, M. C. Luminescence of neutral and ionic gold(I) complexes containing pyrazole or pyrazolate-type ligands. *J. Organomet. Chem.* **2007**, *692*, 1690-1697.

53. Elbjeirami, O.; Rawashdeh-Omary, M. A.; Omary, M. A. Phosphorescence sensitization via heavy-atom effects in d^{10} complexes. *Res. Chem. Intermed.* **2011**, *37*, 691-703.

54. Grimes, T.; Omary, M. A.; Dias, H. V. R.; Cundari, T. R. Intertrimer and intratrimer metallophilic and excimeric bonding in the ground and phosphorescent states of trinuclear coinage metal pyrazolates: A computational study. *J. Phys. Chem. A* **2006**, *110*, 5823-5830.

55. Burini, A.; Galassi, R.; R. Pietroni, B.; Burini, A.; P. Fackler Jr, J.; Galassi, R.; J. Staples, R. The first sandwich silver cluster of a trinuclear cyclic gold(I) complex. *Chem. Commun.* **1998**, 95-96.

56. Burini, A.; Bravi, R.; Fackler, J. P.; Galassi, R.; Grant, T. A.; Omary, M. A.; Pietroni, B. R.; Staples, R. J. Luminescent Chains Formed from Neutral, Triangular Gold Complexes Sandwiching Tl^I and Ag^I. Structures of $\{Ag([Au(\mu\text{-}C^2,N^3\text{-bzim})]_3)_2\}BF_4\cdot CH_2Cl_2$, $\{Tl([Au(\mu\text{-}C^2,N^3\text{-bzim})]_3)_2\}PF6\cdot 0.5THF$ (bzim = 1-Benzylimidazolate), and $\{Tl([Au(\mu\text{-}C(OEt){=}NC_6H_4CH_3)]_3)_2\}PF_6\cdot THF$, with MAu_6 ($M = Ag^+, Tl^+$) Cluster Cores. *Inorg. Chem.* **2000**, *39*, 3158-3165.

57. Ni, W.-X.; Qiu, Y.-M.; Li, M.; Zheng, J.; Sun, R. W.-Y.; Zhan, S.-Z.; Ng, S. W.; Li, D. Metallophilicity-Driven Dynamic Aggregation of a Phosphorescent Gold(I)–Silver(I) Cluster Prepared by Solution-Based and Mechanochemical Approaches. *J. Am. Chem. Soc.* **2014,** *136*, 9532-9535.

58. Upadhyay, P. K.; Marpu, S. B.; Benton, E. N.; Williams, C. L.; Telang, A.; Omary, M. A. A Phosphorescent Trinuclear Gold(I) Pyrazolate Chemosensor for Silver Ion Detection and Remediation in Aqueous Media. *Anal. Chem.* **2018**, *90*, 4999-5006.